View metadata, citation and similar papers at core.ac.uk

brought to you by CORE

provided by DigitalCommons@University of Nebraska

University of Nebraska - Lincoln

DigitalCommons@University of Nebraska - Lincoln

Papers in the Earth and Atmospheric Sciences

Earth and Atmospheric Sciences, Department of

2006

Isopiestic Measurement of the Osmotic Coefficients of Aqueous $\{xH_2SO_4 + (1-x)Fe_2(SO_4)_3\}$ Solutions at 298.15 and 323.15 K

Mariano Velazquez-Rivera
University of Nebraska-Lincoln

Donald Palmer
Oak Ridge National Laboratory

Richard Kettler
University of Nebraska-Lincoln, rkettler1@unl.edu

Follow this and additional works at: https://digitalcommons.unl.edu/geosciencefacpub

Part of the Earth Sciences Commons

Velazquez-Rivera, Mariano; Palmer, Donald; and Kettler, Richard, "Isopiestic Measurement of the Osmotic Coefficients of Aqueous $\{xH_2SO_4 + (1-x)Fe_2(SO_4)_3\}$ Solutions at 298.15 and 323.15 K" (2006). *Papers in the Earth and Atmospheric Sciences*. 78.
https://digitalcommons.unl.edu/geosciencefacpub/78

This Article is brought to you for free and open access by the Earth and Atmospheric Sciences, Department of at DigitalCommons@University of Nebraska - Lincoln. It has been accepted for inclusion in Papers in the Earth and Atmospheric Sciences by an authorized administrator of DigitalCommons@University of Nebraska - Lincoln.

J Solution Chem (2006) 35:1699–1730
DOI 10.1007/s10953-006-9091-4

ORIGINAL PAPER

Isopiestic Measurement of the Osmotic Coefficients of Aqueous $\{x\text{H}_2\text{SO}_4 + (1-x)\text{Fe}_2(\text{SO}_4)_3\}$ Solutions at 298.15 and 323.15 K

Mariano Velázquez-Rivera · Donald A. Palmer · Richard M. Kettler

Received: 7 June 2005 / Accepted: 9 June 2006 / Published online: 7 December 2006
Springer Science+Business Media, LLC 2006

Abstract This study measures the osmotic coefficients of $\{x\text{H}_2\text{SO}_4 + (1-x)\text{Fe}_2(\text{SO}_4)_3\}$(aq) solutions at 298.15 and 323.15 K that have ionic strengths as great as 19.3 mol·kg^{-1}, using the isopiestic method. Experiments utilized both aqueous NaCl and H_2SO_4 as reference solutions. Equilibrium values of the osmotic coefficient obtained using the two different reference solutions were in satisfactory internal agreement. The solutions follow generally the Zdanovskii empirical linear relationship and yield values of a_w for the $Fe_2(SO_4)_3$–H_2O binary system at 298.15 K that are in good agreement with recent work and are consistent with other $M_2(SO_4)_3$–H_2O binary systems.

Keywords Osmotic coefficients · Isopiestic · Iron(III) sulfate · Water activity · Sulfuric acid · Acid-rock drainage

1 Introduction

This study reports the osmotic coefficients of $\{x\text{H}_2\text{SO}_4 + (1-x)\text{Fe}_2(\text{SO}_4)_3\}$(aq) solutions that have ionic strength values as large as 18.3 mol·kg^{-1} at 298.15 K and 19.3 mol·kg^{-1} at 323.15 K.

The oxidation of sulfide minerals can generate significant amounts of acid. Although the process is a complex one, there is general agreement that one of the important reactions is the abiotic oxidation of pyrite by aqueous ferric iron [1].

$$\text{FeS}_2(\text{pyrite}) + 14\text{Fe}^{3+}(\text{aq}) + 8\text{H}_2\text{O(l)} \rightarrow 15\text{Fe}^{2+}(\text{aq}) + 2\text{SO}_4^{2-}(\text{aq}) + 16\text{H}^+(\text{aq}) \quad (1)$$

M. Velázquez-Rivera · R. M. Kettler (✉)
Department of Geosciences, University of Nebraska, Lincoln, Nebraska 68588–0340
D. A. Palmer
Chemical Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008,
Oak Ridge Tennessee 37831–6110

This reaction produces 16 moles of H^+ for every mole of pyrite oxidized and contributes greatly to the acidity of waters in contact with pyrite and other metal sulfides. The supply of ferric iron is typically replenished by the oxidation of aqueous ferrous iron following the reaction

$$Fe^{2+}(aq) + 0.25O_2(g) + H^+(aq) \rightleftarrows Fe^{3+}(aq) + 0.5H_2O(l) \tag{2}$$

and is mediated by species such as *Thiobacillus ferrooxidans* [1].

Acid-sulfate brines can, therefore, be produced where oxygen, water and sulfide minerals combine. These environments include active and abandoned mine workings, waste and tailings [2]; exposed coastal plain sediments [3] or ancient sedimentary rock [4]; and hydrometallurgical operations [5]. Mine workings, wastes and tailings are particularly important localities for the generation of acid rock drainage because these settings combine enhanced permeability to water and air, anomalous concentrations of sulfide minerals and greater surface exposure of sulfides [1]. This combination is so amenable to the generation of acid-sulfate brines that concentrated solutions with pH values as low as –3.6 containing less than 190 g H_2O per liter of solution have been reported [6]. The reactions in Eqs. (1) and (2) are also strongly exothermic. Thus, even within relatively well-ventilated abandoned mine workings, water temperatures may reach 320 K [7] and air temperatures within mine dumps and other accumulations of sulfide-rich rock may approach 338 K [8].

Considerable effort has been devoted to the study of acid-sulfate waters and the minerals formed by these solutions, because of their environmental and economic significance. These efforts have, however, been hampered by a poor understanding of the activities of dissolved species in acidic ferric-sulfate brines. The acid-sulfate brines produced by acid-rock drainage may have ionic strength values that exceed 20 $mol \cdot kg^{-1}$ and cannot be modeled using simple extensions of the Debye-Hückel theory. The interaction parameters necessary for predicting the activities of iron(III), sulfate and hydrogen ions in concentrated solutions can be retrieved from analysis of the osmotic coefficient of acidic iron(III) sulfate aqueous solutions, or the Fe_2O_3-SO_3-H_2O system. The composition of these solutions can be expressed as $\{xH_2SO_4 + (1-x)Fe_2(SO_4)_3\}(aq)$, where x is the mole fraction of $H_2SO_4(aq)$.

The isopiestic method provides a simple and convenient way of measuring the osmotic coefficients of concentrated solutions comprising a non-volatile solute dissolved in a volatile solvent [9] and has been used to quantify activity-composition relationships for a variety of electrolytes including H_2SO_4 [10] and $(NH_4)_2SO_4$ [11]. Both NaCl(aq) and $H_2SO_4(aq)$ are potential standards for isopiestic studies of concentrated $\{xH_2SO_4 + (1-x)Fe_2(SO_4)_3\}(aq)$ solutions. The osmotic and activity coefficients of NaCl(aq) have been measured over a wide range of concentration and temperature [12–16]. The simplicity of the NaCl(aq) system and the accuracy of the data available make it a good candidate for use as a reference solution. On the other hand, although $H_2SO_4(aq)$ is a more complex electrolyte, it is an important component of acid-rock drainage and has been described thermodynamically by a number of workers [17–20]. Clegg *et al.* [17] reviewed a variety of data comprising measurements of the osmotic coefficients, vapor pressure, Emf and degree of dissociation of sulfuric acid solutions and used an extended form of the Pitzer ion-interaction model to model these values over a wide range of concentration (0.0001 to 6.000 $mol \cdot kg^{-1}$) at 273.15, 298.15 and 323.15 K. Using $H_2SO_4(aq)$ and/or NaCl(aq) as reference standards, the osmotic coefficients of concentrated $\{xH_2SO_4 + (1-x)Fe_2(SO_4)_3\}(aq)$ solutions can be measured by the isopiestic method with high precision and accuracy over a wide range of concentration and temperature.

A recent, well-documented, careful study [21] has presented isopiestic data for the $Fe_2(SO_4)_3$–H_2SO_4–H_2O system at 298.15 K and has used these data to retrieve Pitzer parameters for the $Fe_2(SO_4)_3$–H_2O system. These measurements utilized sulfuric acid as a reference solution and exhibited large discrepancies with previous work on the $Fe_2(SO_4)_3$–H_2SO_4–H_2O system [22]. The present study is significant for three reasons. 1) The measurement of isopiestic data at 323.15 K will allow extension of the Pitzer ion-interaction treatment to solutions existing at temperatures typical of many acid-rock drainage systems. 2) The discrepancy between the values published in the two previous studies [21, 22] can be resolved. 3) The current study uses aqueous NaCl as a reference solution for many of the experiments and therefore provides a check on the consistency and accuracy of the results.

2 Experimental

2.1 Materials

Water used in the preparation and standardization of solutions was passed through a Barnsted triple-stage-deionizing unit capable of producing water with a resistivity of 0.18 MΩ·m. A total of four different solutions were prepared: a (0.99945 ± 0.00021) $mol{\cdot}kg^{-1}$ sodium chloride standard solution, a (0.51457 ± 0.00015) $mol{\cdot}kg^{-1}$ sulfuric acid standard solution, and two different $\{xH_2SO_4 + (1-x)Fe_2(SO_4)_3\}(aq)$ solutions where the mole fraction of sulfuric acid, x, was either 0.83424 or 0.74950. These latter two solutions will be referred to as Test Solution 1 and Test Solution 2, respectively (Table 1).

The sodium chloride (Fisher Scientific, ACS reagent grade) solution was prepared as described by Dickson *et al*., [23] purged with argon under acidic conditions to remove carbon dioxide and standardized using the ion exchange/potentiometric titration analysis method. The sulfuric acid solution (EM Science) was used as purchased after standardization by potentiometric and gravimetric techniques.

Test Solution 1 was prepared from iron metal (J.T. Baker), sulfuric acid (J.T. Baker Ultrex II, ultra pure reagent), hydrogen peroxide (EM Science) and purified water. Test Solution 2 was made by combining iron(III) sulfate (Baker and Adamson Allied chemical reagent) sulfuric acid (J.T. Baker Ultrex II, ultra pure reagent) and purified water. Both solutions were filtered individually using 0.22-μm Nylon filters (Fisher Scientific). The sulfate concentration in both solutions was measured using the same gravimetric method as for the sulfuric acid standard solution (Table 1). The total iron concentration in both solutions was obtained by coulometric and potentiometric techniques (Table 1). The total hydrogen ion concentrations in Test Solutions 1 and 2 were obtained through mass-balance calculations (Table 1).

2.2 Apparatus

The isopiestic experiments were performed with the apparatus described originally by Rush *et al.* [24] with modifications noted by Clegg *et al.* [11]. Briefly, the isopiestic apparatus comprises a Plexiglass chamber containing a gold-plated copper block, which provides a uniform temperature buffer. The copper block holds twelve cups arranged around the circumference. The test and standard solutions are contained in platinum cups fitted tightly with chlorotrifluoroethylene (KELF) lids. The cups are threaded into recesses in the block to facilitate heat exchange. The inner walls of the cups are lined with platinum screens to increase the surface area of solution exposed to the atmosphere inside the chamber, which rotates at an angle such that the screens are continually wetted. The chamber is completely

Table 1 Composition of stock Test Solutions 1 and 2 and starting test solution compositions

		$\underline{x}H_2SO_4$	$[SO_4^{2-}]_T/(mol{\cdot}kg^{-1})$	$[Fe^{3+}]_T/(mol{\cdot}kg^{-1})$	$[H^+]_T/(mol{\cdot}kg^{-1})$
Test Solution 1		0.83424	1.9344 ± 0.0037	0.48163 ± 0.00033	2.42391 ± 0.0074
Test Solution 2		0.74950	1.50228 ± 0.00047	0.50143 ± 0.00029	1.50027 ± 0.00094
Exp	Cup				
1	3	0.74950	1.50101 ± 0.00047	0.50100 ± 0.00029	1.49890 ± 0.00094
1	4	0.81512	1.09835 ± 0.00028	0.29649 ± 0.00017	1.30715 ± 0.00057
1	5	0.85552	0.92118 ± 0.00021	0.20651 ± 0.00012	1.22277 ± 0.00043
1	6	0.88609	0.81077 ± 0.00018	0.150438 ± 0.000087	1.17020 ± 0.00035
1	9	0.83424	1.9344 ± 0.0037	0.48163 ± 0.00033	3.8688 ± 0.0074
1	10	0.86441	1.3866 ± 0.0023	0.29579 ± 0.00020	2.7731 ± 0.0045
1	11	0.88191	1.1781 ± 0.0017	0.22508 ± 0.00015	2.3562 ± 0.0035
1	12	0.90851	0.9459 ± 0.0011	0.14630 ± 0.00010	1.8917 ± 0.0023
2	3	0.74950	1.50101 ± 0.00047	0.50100 ± 0.00029	1.49890 ± 0.00094
2	4	0.80457	1.15195 ± 0.00031	0.32372 ± 0.00019	1.33267 ± 0.00062
2	5	0.84139	0.97858 ± 0.00023	0.23567 ± 0.00014	1.25011 ± 0.00047
2	6	0.87425	0.85149 ± 0.00019	0.171116 ± 0.000099	1.18959 ± 0.00038
2	9	0.83424	1.9344 ± 0.0037	0.48163 ± 0.00033	3.8688 ± 0.0074
2	10	0.86390	1.3935 ± 0.0023	0.29816 ± 0.00020	2.7871 ± 0.0046
2	11	0.87875	1.2118 ± 0.0018	0.23650 ± 0.00016	2.4235 ± 0.0036
2	12	0.90720	0.9555 ± 0.0012	0.14958 ± 0.00010	1.9110 ± 0.0023
3	3	0.74950	1.50101 ± 0.00047	0.50100 ± 0.00029	1.49890 ± 0.00094
3	4	0.80515	1.14894 ± 0.00031	0.32219 ± 0.00019	1.33124 ± 0.00061
3	5	0.84083	0.98095 ± 0.00024	0.23687 ± 0.00014	1.25124 ± 0.00047
3	6	0.87542	0.84736 ± 0.00019	0.169021 ± 0.000098	1.18762 ± 0.00037
3	9	0.83424	1.9344 ± 0.0037	0.48163 ± 0.00033	3.8688 ± 0.0074
3	10	0.86877	1.3291 ± 0.0021	0.27632 ± 0.00019	2.6583 ± 0.0042
3	11	0.87859	1.2136 ± 0.0018	0.23711 ± 0.00016	2.4271 ± 0.0036
3	12	0.91005	0.9347 ± 0.0011	0.142513 ± 0.000098	1.8694 ± 0.0022
4	2	0.74950	1.50101 ± 0.00047	0.50100 ± 0.00029	1.49890 ± 0.00094
4	3	0.78026	1.29003 ± 0.00037	0.39385 ± 0.00023	1.39843 ± 0.00074
4	4	0.81860	1.08143 ± 0.00028	0.28790 ± 0.00017	1.29909 ± 0.00056
4	5	0.86314	0.89197 ± 0.00020	0.19168 ± 0.00011	1.20887 ± 0.00040
4	6	0.92340	0.69685 ± 0.00015	0.092579 ± 0.000054	1.11595 ± 0.00030
4	8	0.83424	1.9344 ± 0.0037	0.48163 ± 0.00033	3.8688 ± 0.0074
4	9	0.85276	1.5623 ± 0.0027	0.35540 ± 0.00024	3.1246 ± 0.0055
4	10	0.86882	1.3286 ± 0.0021	0.27614 ± 0.00019	2.6572 ± 0.0042
4	11	0.89084	1.0908 ± 0.0015	0.19547 ± 0.00013	2.1816 ± 0.0030
4	12	0.93673	0.76932 ± 0.00068	0.086415 ± 0.000059	1.5386 ± 0.0014
6	2	0.74950	1.50101 ± 0.00047	0.50100 ± 0.00029	1.49890 ± 0.00094
6	3	0.92612	0.68930 ± 0.00015	0.088742 ± 0.000051	1.11235 ± 0.00030
6	4	0.86602	0.88128 ± 0.00020	0.18625 ± 0.00011	1.20377 ± 0.00040
6	5	0.81877	1.08058 ± 0.00028	0.28747 ± 0.00017	1.29868 ± 0.00055
6	6	0.78206	1.27904 ± 0.00037	0.38826 ± 0.00022	1.39319 ± 0.00073
6	8	0.83424	1.9344 ± 0.0037	0.48163 ± 0.00033	3.8688 ± 0.0074
6	9	0.85053	1.6004 ± 0.0028	0.36832 ± 0.00025	3.2007 ± 0.0057
6	10	0.87082	1.3036 ± 0.0021	0.26764 ± 0.00018	2.6072 ± 0.0041
6	11	0.89664	1.0396 ± 0.0014	0.17809 ± 0.00012	2.0791 ± 0.0027
6	12	0.93736	0.76598 ± 0.00067	0.085283 ± 0.000058	1.5320 ± 0.0013

immersed in a thermostatted water bath, which maintains the temperature to within 0.005 K of the set point

2.3 Experimental procedure

The masses of the capped platinum cups and the solutions contained within were measured over time during the experiments. The initial data recorded were, therefore, the masses of the empty capped cups and the corresponding masses after aliquots of the test and standard solutions had been added. Pairs of reference standards (sulfuric acid and/or sodium chloride) were located on opposite sides of the block. Half of the remaining empty cups, or test cups, contained similar amounts of Test Solution 1, whereas the other half contained Test Solution 2. Differing amounts of sulfuric acid were added to each set of the test cups to prepare solutions having different ratios of H_2SO_4 to $Fe_2(SO_4)_3$. Thus, each of the test cups contained a different $\{x\mathrm{H_2SO_4} + (1-x)\mathrm{Fe_2(SO_4)_3}\}$(aq) solution for which the value of x remained constant during each experiment (Table 1).

The following steps summarize the experimental procedure and sampling process. 1) After initially weighing the cups as described above to ascertain the mass of the initial solutions, the cups were fitted into the copper block inside the chamber. 2) The chamber was closed and evacuated to remove air and promote solvent distillation. 3) The lids were then raised using an internal hoist, the chamber was immersed in the water bath, tilted at an angle of *ca.* 15° to horizontal, and rotated at 30 rpm to accelerate the equilibration process. Equilibrium was achieved by distillation of solvent from solutions with high water activity to solutions with low water activity until the activity of water was the same for all the solutions within the system. 4) Measurements were made by weighing the cups periodically (sampling). The chamber was removed from the water bath and the lids were lowered immediately to prevent solvent evaporation. Ultra-pure nitrogen (99.999%) was bled into the chamber through vents located around the underside of the chamber lid so that the chamber lid could be removed. The capped cups were then placed on a metal tray to facilitate thermal equilibration to room temperature whereupon the cups were weighed. 5) Steps 2 through 4 were repeated after either adding a known mass of purified water to the center of the block or removing a known mass of condensed vapor from the sealed chamber during evacuation to obtain a different set of compositions at lower or higher concentrations, respectively. 6) Finally, the temperature of the water bath was increased from 298.15 to 323.15 K or the cups were removed from the chamber to conclude the experiment and a new experiment was initiated.

The weighing process (sampling) was repeated periodically at both temperatures, allowing the system to equilibrate between sampling episodes. The time allowed for the system to reach equilibrium ranged from 2 to 4 weeks at 298.15 K whereas the time allowed for equilibration ranged from 1 to 4 weeks at 323.15 K. That the system attained isopiestic equilibrium could only be ascertained after weighing the cups and calculating the new solution compositions. The system was considered to be at equilibrium if the value of a_w among the different standard solutions in the system agreed to within 0.1%. A discrepancy between the sodium chloride concentrations in the two standard cups was considered to be evidence of precipitate formation in one of the cups. Precipitates were re-dissolved by the addition of water to the system. Five different experiments were performed and they are referred to as Experiments 1, 2, 3, 4 and 6. Experiments 1, 2, and 3 were conducted using both sodium chloride and sulfuric acid as reference standards. Thus four of the cups (cup numbers 1, 2, 7, and 8) were occupied with standard solutions, whereas the remaining eight cups were filled with test solutions. Experiment 4 used aqueous sodium chloride as the only reference standard; and Experiment 6 utilized aqueous sulfuric acid as the only reference standard. In these latter two experiments two of the cups (cup numbers 1 and 7) were occupied with standard solutions whereas the remaining ten were filled with test solutions. The mole fraction of sulfuric acid (x) and the initial total sulfate, iron(III) and hydrogen ion concentrations in each test cup are presented in Table 1. All measurements of mass were corrected for solution buoyancy. Densities of the sulfuric acid and sodium chloride standards were calculated using published relations [25]. The densities of Test Solutions 1 and 2 were measured to be $1.1488 \pm 0.0010\ \mathrm{g{\cdot}cm^{-3}}$ and $1.2620 \pm 0.0015\ \mathrm{g{\cdot}cm^{-3}}$, respectively and were assumed to be independent of temperature from 295 to 325 K.

3 Results

The activity of water, a_w, is related to the solution stoichiometric osmotic coefficient, ϕ_S, by the relationship,

$$a_\mathrm{W} = e^{-\frac{\phi_S M_W v_i m_i}{1000}} \tag{3}$$

where M_w is the molar mass of water ($18.015\ \mathrm{g{\cdot}mol^{-1}}$) [26], v_i is the stoichiometric ionization number of electrolyte i ($v_i = 2$ for sodium chloride, 3 for sulfuric acid, and 5 for iron(III) sulfate) and m_i is the stoichiometric molal concentration of electrolyte i. At isopiestic equilibrium, the value of a_w is the same in all solutions. The value of ϕ_S of the $\{x\mathrm{H_2SO_4} + (1-x)\mathrm{Fe_2(SO_4)_3}\}$(aq) solutions can be calculated by rearranging Eq. (3) into the fundamental equation for isopiestic equilibrium,

$$\phi_S = \frac{v_\mathrm{Std} m_\mathrm{Std} \phi_\mathrm{Std}}{\sum\limits_i v_i m_i} = \frac{v_\mathrm{Std} m_\mathrm{Std} \phi_\mathrm{Std}}{(5 - 2X) m_\mathrm{T}} \tag{4}$$

where m_T is the total molality of the mixed electrolyte solution, and m_1 and m_2 are the molal concentrations of sulfuric acid and iron(III) sulfate, respectively. All other terms were defined in Eq. (3) with quantities relevant to the isopiestic reference standard solutions denoted by the subscript Std whereas quantities relevant to the test solution are designated by the S or i subscripts. Values of ϕ_Std for the standard solutions were calculated from extended Pitzer models for sodium chloride {Eq. (7) of Archer [12]) and sulfuric acid (Eq. (11) of Clegg *et al.* [17]}. Compositions of the standard solutions and values of a_w and ϕ_Std obtained in experiments at 298.15 and 323.15 K are presented in Tables 2 and 3, respectively.

It is assumed in this study that iron(III), sulfate and hydrogen ions are the only species present in the $\{x\mathrm{H_2SO_4} + (1-x)\mathrm{Fe_2(SO_4)_3}\}$(aq) solutions. The solution stoichiometric ionic strength designated by I_S is, therefore, given by Eq. (5):

$$I_S = 3m_1 + 15m_2 = (15 - 12x)m_\mathrm{T} \tag{5}$$

The interaction of the different electrolytes in solution and the Fe(II)/Fe(III) ratio will be considered during the modeling in ongoing experiments on the Fe(III)–Fe(II)–$\mathrm{H_2SO_4}$–$\mathrm{H_2O}$ system.

An analysis of error propagation was applied to quantify the uncertainties in solution composition as well as in values of a_w, ϕ_Std and ϕ_S. This exercise incorporated the uncertainties in solution composition noted previously for the standard and test solutions, as well as un-

Table 2 Results of isopiestic measurements at 298.15 K

	Experiment = 1	Sample = 1	[a] $a_W = 0.965402 \pm 0.000011$
[b] Cup	[c] [Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1NaCl	1.04038 ± 0.00022	0.965421 ± 0.000010	0.93881 ± 0.00020
7NaCl	1.04054 ± 0.00022	0.965416 ± 0.000010	0.93882 ± 0.00020
2H_2SO_4	0.91728 ± 0.00027	0.965386 ± 0.000031	0.71062 ± 0.00062
8H_2SO_4	0.91724 ± 0.00027	0.965387 ± 0.000031	0.71061 ± 0.00062
Cup	[d] [$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[e] [H_2SO_4]/(mol·kg^{-1})	ϕ_s
3	0.21495 ± 0.00012	0.64314 ± 0.00055	0.65030 ± 0.00040
4	0.161347 ± 0.000093	0.71137 ± 0.00042	0.66430 ± 0.00033
5	0.127393 ± 0.000074	0.75434 ± 0.00034	0.67365 ± 0.00029
6	0.101259 ± 0.000059	0.78768 ± 0.00029	0.68085 ± 0.00026
9	0.144601 ± 0.000099	0.7277 ± 0.0022	0.6722 ± 0.0016
10	0.119325 ± 0.000082	0.7607 ± 0.0019	0.6786 ± 0.0013
11	0.104487 ± 0.000072	0.7803 ± 0.0016	0.6823 ± 0.0012
12	0.081561 ± 0.000056	0.8099 ± 0.0013	0.68848 ± 0.00094
	Experiment = 1	Sample = 2	$a_W = 0.9759067 \pm 0.0000078$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1NaCl	0.72928 ± 0.00015	0.9759244 ± 0.0000068	0.92748 ± 0.00018
7NaCl	0.72902 ± 0.00015	0.9759330 ± 0.0000068	0.92748 ± 0.00018
2H_2SO_4	0.65819 ± 0.00019	0.975884 ± 0.000022	0.68627 ± 0.00060
8H_2SO_4	0.65815 ± 0.00019	0.975886 ± 0.000022	0.68626 ± 0.00060
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
3	0.158530 ± 0.000092	0.47433 ± 0.00041	0.61045 ± 0.00037
4	0.118175 ± 0.000068	0.52102 ± 0.00031	0.62794 ± 0.00030
5	0.092887 ± 0.000054	0.55002 ± 0.00025	0.63965 ± 0.00026
6	0.073593 ± 0.000043	0.57247 ± 0.00021	0.64858 ± 0.00024
9	0.105710 ± 0.000072	0.5320 ± 0.0016	0.6366 ± 0.0015
10	0.086944 ± 0.000060	0.5543 ± 0.0013	0.6448 ± 0.0013
11	0.075984 ± 0.000052	0.5675 ± 0.0012	0.6495 ± 0.0011
12	0.059143 ± 0.000041	0.58730 ± 0.00092	0.65734 ± 0.00089
	Experiment = 1	Sample = 3	$a_W = 0.9833902 \pm 0.0000053$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1NaCl	0.50741 ± 0.00011	0.9832863 ± 0.0000046	0.92195 ± 0.00017
7NaCl	0.50189 ± 0.00011	0.9834684 ± 0.0000045	0.92186 ± 0.00017
2H_2SO_4	0.46164 ± 0.00013	0.983376 ± 0.000015	0.67193 ± 0.00057
8H_2SO_4	0.46017 ± 0.00013	0.983430 ± 0.000015	0.67185 ± 0.00057
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
3	0.113463 ± 0.000066	0.33949 ± 0.00029	0.58676 ± 0.00035
4	0.083901 ± 0.000049	0.36991 ± 0.00022	0.60845 ± 0.00029
5	0.065702 ± 0.000038	0.38905 ± 0.00018	0.62212 ± 0.00025
6	0.051934 ± 0.000030	0.40399 ± 0.00015	0.63227 ± 0.00022
9	0.075185 ± 0.000052	0.3784 ± 0.0012	0.6158 ± 0.0014
10	0.061541 ± 0.000042	0.39234 ± 0.00095	0.6267 ± 0.0012
11	0.053732 ± 0.000037	0.40129 ± 0.00083	0.6319 ± 0.0011
12	0.041699 ± 0.000029	0.41408 ± 0.00065	0.64139 ± 0.00087

Table 2 Continued

	Experiment = 1	Sample = 4	$a_W = 0.9828852 \pm 0.0000055$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1NaCl	0.51901 ± 0.00011	0.9829038 ± 0.0000047	0.92216 ± 0.00017
7NaCl	0.51756 ± 0.00011	0.9829515 ± 0.0000047	0.92213 ± 0.00017
2H_2SO_4	0.47641 ± 0.00014	0.982826 ± 0.000015	0.67284 ± 0.00058
8H_2SO_4	0.47549 ± 0.00014	0.982860 ± 0.000015	0.67279 ± 0.00058
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
3	0.116976 ± 0.000068	0.35000 ± 0.00030	0.58467 ± 0.00035
4	0.086739 ± 0.000050	0.38243 ± 0.00022	0.60461 ± 0.00029
5	0.067961 ± 0.000039	0.40242 ± 0.00018	0.61785 ± 0.00025
6	0.053671 ± 0.000031	0.41750 ± 0.00016	0.62851 ± 0.00022
9	0.077313 ± 0.000053	0.3891 ± 0.0012	0.6152 ± 0.0014
10	0.063508 ± 0.000044	0.40488 ± 0.00098	0.6239 ± 0.0012
11	0.055455 ± 0.000038	0.41415 ± 0.00086	0.6290 ± 0.0011
12	0.043085 ± 0.000030	0.42785 ± 0.00067	0.63768 ± 0.00086
	Experiment = 2	Sample = 2	$a_W = 0.966801 \pm 0.000011$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1NaCl	1.00039 ± 0.00021	0.9667845 ± 0.0000097	0.93719 ± 0.00020
7NaCl	0.99959 ± 0.00021	0.9668118 ± 0.0000097	0.93716 ± 0.00020
2H_2SO_4	0.88333 ± 0.00026	0.966805 ± 0.000030	0.70715 ± 0.00062
8H_2SO_4	0.88333 ± 0.00026	0.966805 ± 0.000030	0.70715 ± 0.00062
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
3	0.20771 ± 0.00012	0.62148 ± 0.00053	0.64566 ± 0.00040
4	0.164082 ± 0.000095	0.67553 ± 0.00042	0.65835 ± 0.00034
5	0.134390 ± 0.000078	0.71292 ± 0.00036	0.66685 ± 0.00030
6	0.107424 ± 0.000062	0.74683 ± 0.00030	0.67480 ± 0.00027
9	0.139582 ± 0.000096	0.7025 ± 0.0022	0.6681 ± 0.0016
10	0.115550 ± 0.000079	0.7335 ± 0.0018	0.6747 ± 0.0013
11	0.103354 ± 0.000071	0.7491 ± 0.0016	0.6781 ± 0.0012
12	0.079783 ± 0.000055	0.7800 ± 0.0012	0.68435 ± 0.00094
	Experiment = 2	Sample = 3	$a_W = 0.965280 \pm 0.000011$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1NaCl	1.04476 ± 0.00022	0.965272 ± 0.000010	0.93899 ± 0.00020
7NaCl	1.04476 ± 0.00022	0.965272 ± 0.000010	0.93899 ± 0.00020
2H_2SO_4	0.91949 ± 0.00027	0.965293 ± 0.000032	0.71084 ± 0.00062
8H_2SO_4	0.91969 ± 0.00027	0.965284 ± 0.000032	0.71086 ± 0.00062
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
3	0.21539 ± 0.00012	0.64445 ± 0.00055	0.65178 ± 0.00041
4	0.170365 ± 0.000099	0.70140 ± 0.00044	0.66374 ± 0.00035
5	0.139586 ± 0.000081	0.74048 ± 0.00037	0.67207 ± 0.00031
6	0.111647 ± 0.000065	0.77618 ± 0.00031	0.67966 ± 0.00027
9	0.144936 ± 0.000099	0.7294 ± 0.0022	0.6736 ± 0.0016
10	0.119989 ± 0.000082	0.7616 ± 0.0019	0.6801 ± 0.0013
11	0.107376 ± 0.000074	0.7782 ± 0.0017	0.6833 ± 0.0012
12	0.083211 ± 0.000057	0.8135 ± 0.0013	0.68686 ± 0.00095

Table 2 Continued

	Experiment = 2	Sample = 4	$a_w = 0.960186 \pm 0.000012$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1NaCl	1.19337 ± 0.00025	0.960167 ± 0.000012	0.94537 ± 0.00021
7NaCl	1.19340 ± 0.00025	0.960166 ± 0.000012	0.94537 ± 0.00021
$2H_2SO_4$	1.03840 ± 0.00030	0.960208 ± 0.000036	0.72354 ± 0.00063
$8H_2SO_4$	1.03857 ± 0.00030	0.960201 ± 0.000036	0.72356 ± 0.00063
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
3	0.24022 ± 0.00014	0.71874 ± 0.00061	0.67208 ± 0.00042
4	0.19047 ± 0.00011	0.78417 ± 0.00049	0.68274 ± 0.00036
5	0.156339 ± 0.000090	0.82935 ± 0.00041	0.69008 ± 0.00032
6	0.125253 ± 0.000073	0.87078 ± 0.00035	0.69672 ± 0.00029
9	0.16226 ± 0.00011	0.8166 ± 0.0025	0.6919 ± 0.0016
10	0.134554 ± 0.000092	0.8541 ± 0.0021	0.6975 ± 0.0014
11	0.120488 ± 0.000083	0.8732 ± 0.0019	0.7003 ± 0.0012
12	0.093514 ± 0.000064	0.9142 ± 0.0015	0.70288 ± 0.00097
	Experiment = 2	Sample = 5	$a_W = 0.949562 \pm 0.000015$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1NaCl	1.49743 ± 0.00031	0.949534 ± 0.000015	0.95982 ± 0.00022
7NaCl	1.49751 ± 0.00031	0.949531 ± 0.000015	0.95983 ±0.00022
$2H_2SO_4$	1.27419 ± 0.00037	0.949609 ± 0.000044	0.75084 ± 0.00063
$8H_2SO_4$	1.27495 ± 0.00037	0.949574 ± 0.000044	0.75093 ± 0.00063
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
3	0.28785 ± 0.00017	0.86127 ± 0.00074	0.71453 ± 0.00046
4	0.22939 ± 0.00013	0.94441 ± 0.00059	0.72223 ± 0.00040
5	0.18888 ± 0.00011	1.00197 ± 0.00050	0.72770 ± 0.00035
6	0.151790 ± 0.000088	1.05527 ± 0.00043	0.73243 ± 0.00032
10	0.16288 ± 0.00011	1.0339 ± 0.0025	0.7341 ± 0.0014
11	0.14606 ± 0.00010	1.0586 ± 0.0023	0.7359 ± 0.0013
12	0.113683 ± 0.000078	1.1114 ± 0.0018	0.7366 ± 0.0010
	Experiment = 3	Sample = 1	$a_W = 0.964054 \pm 0.000011$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1NaCl	1.08315 ± 0.00023	0.963959 ± 0.000011	0.94059 ± 0.00020
7NaCl	1.08323 ± 0.00023	0.963956 ± 0.000011	0.94059 ± 0.00020
$2H_2SO_4$	0.94712 ± 0.00028	0.964126 ± 0.000033	0.71372 ± 0.00063
$8H_2SO_4$	0.94600 ± 0.00028	0.964174 ± 0.000033	0.71360 ± 0.00063
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
3	0.22143 ± 0.00013	0.66252 ± 0.00057	0.65845 ± 0.00041
4	0.17477 ± 0.00010	0.72215 ± 0.00045	0.67023 ± 0.00035
5	0.144086 ± 0.000083	0.76115 ± 0.00038	0.67835 ± 0.00031
6	0.113849 ± 0.000066	0.79998 ± 0.00032	0.68627 ± 0.00028
9	0.14919 ± 0.00010	0.7508 ± 0.0023	0.6796 ± 0.0016
10	0.119229 ± 0.000082	0.7894 ± 0.0018	0.6874 ± 0.0013
11	0.110650 ± 0.000076	0.8007 ± 0.0017	0.6895 ± 0.0012
12	0.082748 ± 0.000057	0.8372 ± 0.0013	0.69657 ± 0.00093

Table 2 Continued

	Experiment = 3	Sample = 2	$a_W = 0.951462 \pm 0.000014$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1NaCl	1.44721 ± 0.00030	0.951308 ± 0.000015	0.95732 ± 0.00021
7NaCl	1.44716 ± 0.00030	0.951310 ± 0.000015	0.95732 ± 0.00021
2H_2SO_4	1.23138 ± 0.00036	0.951586 ± 0.000042	0.74570 ± 0.00063
8H_2SO_4	1.23007 ± 0.00036	0.951645 ± 0.000042	0.74555 ± 0.00063
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
3	0.27963 ± 0.00016	0.83668 ± 0.00071	0.70898 ± 0.00046
4	0.22206 ± 0.00013	0.91758 ± 0.00057	0.71727 ± 0.00039
5	0.18377 ± 0.00011	0.97081 ± 0.00049	0.72321 ± 0.00035
6	0.145761 ± 0.000084	1.02422 ± 0.00041	0.72888 ± 0.00031
9	0.19020 ± 0.00013	0.9572 ± 0.0029	0.7248 ± 0.0017
10	0.15255 ± 0.00010	1.0100 ± 0.0024	0.7306 ± 0.0014
11	0.141756 ± 0.000097	1.0258 ± 0.0022	0.7318 ± 0.0013
12	0.106406 ± 0.000073	1.0765 ± 0.0017	0.73660 ± 0.00099
	Experiment = 3	Sample = 3	$a_W = 0.930721 \pm 0.000018$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1NaCl	2.02373 ± 0.00043	0.930480 ± 0.000021	0.98821 ± 0.00023
7NaCl	2.02355 ± 0.00043	0.930487 ± 0.000021	0.98820 ± 0.00023
2H_2SO_4	1.65682 ± 0.00048	0.930910 ± 0.000056	0.79955 ± 0.00062
8H_2SO_4	1.65492 ± 0.00048	0.931007 ± 0.000055	0.79930 ± 0.00062
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
3	0.36190 ± 0.00021	1.08281 ± 0.00093	0.79075 ± 0.00054
4	0.28954 ± 0.00017	1.19641 ± 0.00075	0.79405 ± 0.00046
5	0.24083 ± 0.00014	1.27222 ± 0.00064	0.79659 ± 0.00042
6	0.19208 ± 0.00011	1.34967 ± 0.00054	0.79841 ± 0.00039
9	0.24904 ± 0.00017	1.2534 ± 0.0039	0.7991 ± 0.0019
10	0.20075 ± 0.00014	1.3290 ± 0.0031	0.8014 ± 0.0015
11	0.18683 ± 0.00013	1.3520 ± 0.0029	0.8015 ± 0.0014
12	0.140940 ± 0.000097	1.4259 ± 0.0022	0.8027 ± 0.0011
	Experiment = 3	Sample = 4	$a_W = 0.902296 \pm 0.000022$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1NaCl	2.76992 ± 0.00058	0.901980 ± 0.000030	1.03371 ± 0.00025
7NaCl	2.76958 ± 0.00058	0.901993 ± 0.000030	1.03369 ± 0.00025
2H_2SO_4	2.17767 ± 0.00063	0.902528 ± 0.000071	0.87140 ± 0.00061
8H_2SO_4	2.17496 ± 0.00063	0.902684 ± 0.000070	0.87102 ± 0.00061
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
3	0.45741 ± 0.00026	1.3686 ± 0.0012	0.89571 ± 0.00066
4	0.36861 ± 0.00021	1.52316 ± 0.00095	0.89296 ± 0.00058
5	0.30820 ± 0.00018	1.62810 ± 0.00081	0.89119 ± 0.00054
6	0.24707 ± 0.00014	1.73609 ± 0.00070	0.88866 ± 0.00050
9	0.31833 ± 0.00022	1.6020 ± 0.0049	0.8950 ± 0.0021
10	0.25794 ± 0.00018	1.7076 ± 0.0040	0.8930 ± 0.0017
11	0.24041 ± 0.00016	1.7396 ± 0.0037	0.8918 ± 0.0016
12	0.18225 ± 0.00012	1.8439 ± 0.0028	0.8888 ± 0.0012

Table 2 Continued

	Experiment = 3	Sample = 5	$a_W = 0.873427 \pm 0.000025$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1NaCl	3.48509 ± 0.00073	0.873021 ± 0.000038	1.08147 ± 0.00026
7NaCl	3.48506 ± 0.00073	0.873022 ± 0.000038	1.08146 ± 0.00026
2H_2SO_4	2.65468 ± 0.00077	0.873744 ± 0.000084	0.94074 ± 0.00061
8H_2SO_4	2.65187 ± 0.00077	0.873920 ± 0.000084	0.94032 ± 0.00061
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
3	0.54198 ± 0.00031	1.6216 ± 0.0014	0.99514 ± 0.00080
4	0.43892 ± 0.00025	1.8137 ± 0.0011	0.98721 ± 0.00072
5	0.36827 ± 0.00021	1.94546 ± 0.00097	0.98180 ± 0.00067
6	0.29632 ± 0.00017	2.08217 ± 0.00083	0.97539 ± 0.00063
9	0.38019 ± 0.00026	1.9134 ± 0.0059	0.9865 ± 0.0024
10	0.30917 ± 0.00021	2.0469 ± 0.0048	0.9807 ± 0.0019
11	0.28836 ± 0.00020	2.0866 ± 0.0045	0.9788 ± 0.0018
12	0.21951 ± 0.00015	2.2208 ± 0.0034	0.9714 ± 0.0014
	Experiment = 3	Sample = 6	$a_W = 0.814983 \pm 0.000028$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1NaCl	4.8338 ± 0.0010	0.814347 ± 0.000053	1.17920 ± 0.00028
7NaCl	4.8330 ± 0.0010	0.814384 ± 0.000053	1.17914 ± 0.00028
2H_2SO_4	3.5182 ± 0.0010	0.81549 ± 0.00011	1.07272 ± 0.00062
8H_2SO_4	3.5151 ± 0.0010	0.81571 ± 0.00011	1.07223 ± 0.00062
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
3	0.69270 ± 0.00040	2.0726 ± 0.0018	1.1774 ± 0.0011
4	0.56433 ± 0.00033	2.3319 ± 0.0015	1.1611 ± 0.0010
5	0.47549 ± 0.00028	2.5118 ± 0.0013	1.14988 ± 0.00097
6	0.38440 ± 0.00022	2.7011 ± 0.0011	1.13701 ± 0.00093
9	0.49058 ± 0.00034	2.4690 ± 0.0076	1.1561 ± 0.0028
10	0.40061 ± 0.00027	2.6522 ± 0.0062	1.1445 ± 0.0023
11	0.37438 ± 0.00026	2.7091 ± 0.0058	1.1400 ± 0.0022
12	0.28621 ± 0.00020	2.8957 ± 0.0045	1.1266 ± 0.0017
	Experiment = 3	Sample = 8	$a_W = 0.797765 \pm 0.000029$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1NaCl	5.2126 ± 0.0011	0.797020 ± 0.000057	1.20802 ± 0.00028
7NaCl	5.2102 ± 0.0011	0.797131 ± 0.000057	1.20784 ± 0.00028
2H_2SO_4	3.7546 ± 0.0011	0.79833 ± 0.00011	1.11000 ± 0.00063
8H_2SO_4	3.7512 ± 0.0011	0.79858 ± 0.00011	1.10946 ± 0.00063
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
3	0.73374 ± 0.00042	2.1954 ± 0.0019	1.2277 ± 0.0012
4	0.59849 ± 0.00035	2.4731 ± 0.0015	1.2092 ± 0.0011
5	0.50475 ± 0.00029	2.6664 ± 0.0013	1.1964 ± 0.0011
6	0.40843 ± 0.00024	2.8699 ± 0.0011	1.1820 ± 0.0010
9	0.52042 ± 0.00036	2.6191 ± 0.0081	1.2037 ± 0.0030
10	0.42551 ± 0.00029	2.8171 ± 0.0066	1.1901 ± 0.0024
11	0.39766 ± 0.00027	2.8775 ± 0.0062	1.1854 ± 0.0023
12	0.30436 ± 0.00021	3.0793 ± 0.0047	1.1701 ± 0.0018

Table 2 Continued

	Experiment = 3	Sample = 9	$a_W = 0.855362 \pm 0.000026$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1NaCl	3.91479 ± 0.00082	0.854877 ± 0.000043	1.11166 ± 0.00026
7NaCl	3.91438 ± 0.00082	0.854895 ± 0.000043	1.11163 ± 0.00026
2H_2SO_4	2.93380 ± 0.00086	0.855741 ± 0.000092	0.98255 ± 0.00061
8H_2SO_4	2.93087 ± 0.00085	0.855934 ± 0.000092	0.98210 ± 0.00061
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
3	0.59071 ± 0.00034	1.7674 ± 0.0015	1.05420 ± 0.00089
4	0.47953 ± 0.00028	1.9815 ± 0.0012	1.04330 ± 0.00081
5	0.40305 ± 0.00023	2.1292 ± 0.0011	1.03575 ± 0.00076
6	0.32490 ± 0.00019	2.28298 ±0.00091	1.02712 ± 0.00072
9	0.41587 ± 0.00028	2.0930 ± 0.0064	1.0413 ± 0.0025
10	0.33879 ± 0.00023	2.2429 ± 0.0053	1.0333 ± 0.0020
11	0.31626 ± 0.00022	2.2886 ± 0.0049	1.0303 ± 0.0019
12	0.24030 ± 0.00016	2.4312 ± 0.0037	1.0245 ± 0.0015
	Experiment = 3	Sample = 10	$a_W = 0.898801 \pm 0.000022$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1NaCl	2.85868 ± 0.00060	0.898473 ± 0.000031	1.03944 ± 0.00025
7NaCl	2.85828 ± 0.00060	0.898488 ± 0.000031	1.03942 ± 0.00025
2H_2SO_4	2.23764 ± 0.00065	0.899052 ± 0.000072	0.87996 ± 0.00061
8H_2SO_4	2.23526 ± 0.00065	0.899190 ± 0.000072	0.87962 ± 0.00061
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
3	0.46816 ± 0.00027	1.4008 ± 0.0012	0.90820 ± 0.00068
4	0.37752 ± 0.00022	1.55995 ± 0.00097	0.90483 ± 0.00060
5	0.31581 ± 0.00018	1.66828 ± 0.00083	0.90256 ± 0.00055
6	0.25328 ± 0.00015	1.77972 ± 0.00071	0.89960 ± 0.00052
9	0.32615 ± 0.00022	1.6414 ± 0.0051	0.9065 ± 0.0021
10	0.26444 ± 0.00018	1.7507 ± 0.0041	0.9039 ± 0.0017
11	0.24647 ± 0.00017	1.7835 ± 0.0038	0.9027 ± 0.0016
12	0.18698 ± 0.00013	1.8917 ± 0.0029	0.8990 ± 0.0013
	Experiment = 3	Sample = 11	$a_W = 0.920785 \pm 0.000020$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1NaCl	2.28908 ± 0.00048	0.920548 ± 0.000024	1.00378 ± 0.00024
7NaCl	2.28937 ± 0.00048	0.920537 ± 0.000024	1.00380 ± 0.00024
2H_2SO_4	1.84606 ± 0.00054	0.920980 ± 0.000061	0.82507 ± 0.00062
8H_2SO_4	1.84429 ± 0.00054	0.921075 ± 0.000061	0.82483 ± 0.00062
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
3	0.39707 ± 0.00023	1.1881 ± 0.0010	0.82815 ± 0.00058
4	0.31858 ± 0.00018	1.31642 ± 0.00082	0.82924 ± 0.00050
5	0.26560 ± 0.00015	1.40307 ± 0.00070	0.82998 ± 0.00046
6	0.21224 ± 0.00012	1.49137 ± 0.00060	0.83027 ± 0.00042
9	0.27441 ± 0.00019	1.3810 ± 0.0043	0.8333 ± 0.0020
10	0.22173 ± 0.00015	1.4679 ± 0.0034	0.8337 ± 0.0016
11	0.20642 ± 0.00014	1.4937 ± 0.0032	0.8336 ± 0.0015
12	0.15605 ± 0.00011	1.5788 ± 0.0024	0.8331 ± 0.0011

Table 2 Continued

	Experiment = 3	Sample = 12	$a_W = 0.939890 \pm 0.000017$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1NaCl	1.77174 ± 0.00037	0.939709 ± 0.000018	0.97416 ± 0.00022
7NaCl	1.77194 ± 0.00037	0.939701 ± 0.000018	0.97417 ± 0.00022
2H_2SO_4	1.47470 ± 0.00043	0.940042 ± 0.000050	0.77580 ± 0.00063
8H_2SO_4	1.47333 ± 0.00043	0.940109 ± 0.000050	0.77563 ± 0.00063
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
3	0.32723 ± 0.00019	0.97910 ± 0.00084	0.75482 ± 0.00050
4	0.26099 ± 0.00015	1.07843 ± 0.00067	0.76034 ± 0.00043
5	0.21670 ± 0.00013	1.14475 ± 0.00057	0.76413 ± 0.00039
6	0.172455 ± 0.000100	1.21179 ± 0.00049	0.76754 ± 0.00035
9	0.22405 ± 0.00015	1.1276 ± 0.0035	0.7666 ± 0.0018
10	0.18030 ± 0.00012	1.1937 ± 0.0028	0.7701 ± 0.0015
11	0.16766 ± 0.00011	1.2132 ± 0.0026	0.7709 ± 0.0014
12	0.126230 ± 0.000086	1.2771 ± 0.0020	0.7736 ± 0.0011
	Experiment = 4	Sample = 1	$a_W = 0.9581417 \pm 0.0000084$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1NaCl	1.25195 ± 0.00026	0.958139 ± 0.000012	0.94802 ± 0.00021
7NaCl	1.25179 ± 0.00026	0.958144 ± 0.000012	0.94801 ± 0.00021
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
2	0.24775 ± 0.00014	0.74128 ± 0.00063	0.68549 ± 0.00043
3	0.21958 ± 0.00013	0.77971 ± 0.00056	0.69060 ± 0.00040
4	0.18364 ± 0.00011	0.82869 ± 0.00048	0.69723 ± 0.00035
5	0.140705 ± 0.000081	0.88742 ± 0.00038	0.70521 ± 0.00031
6	0.080437 ± 0.000047	0.96961 ± 0.00030	0.71688 ± 0.00026
8	0.16727 ± 0.00011	0.8418 ± 0.0026	0.7060 ± 0.0016
9	0.14967 ± 0.00010	0.8668 ± 0.0023	0.7088 ± 0.0015
10	0.134222 ± 0.000092	0.8889 ± 0.0021	0.7111 ± 0.0013
11	0.112716 ± 0.000077	0.9199 ± 0.0018	0.7143 ± 0.0011
12	0.066568 ± 0.000046	0.9856 ± 0.0010	0.72156 ± 0.00071
	Experiment = 4	Sample = 2	$a_W = 0.925475 \pm 0.000015$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1NaCl	2.15802 ± 0.00045	0.925481 ± 0.000023	0.99600 ± 0.00023
7NaCl	2.15834 ± 0.00045	0.925469 ± 0.000023	0.99602 ± 0.00023
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
2	0.37745 ± 0.00022	1.12934 ± 0.00096	0.81496 ± 0.00056
3	0.33664 ± 0.00019	1.19537 ± 0.00086	0.81588 ± 0.00052
4	0.28392 ± 0.00016	1.28122 ± 0.00074	0.81682 ± 0.00047
5	0.21978 ± 0.00013	1.38613 ± 0.00060	0.81775 ± 0.00042
6	0.127569 ± 0.000074	1.53776 ± 0.00047	0.81871 ± 0.00037
8	0.25992 ± 0.00018	1.3081 ± 0.0040	0.8230 ± 0.0019
9	0.23353 ± 0.00016	1.3525 ± 0.0036	0.8228 ± 0.0017
10	0.21016 ± 0.00014	1.3918 ± 0.0033	0.8226 ± 0.0016
11	0.17741 ± 0.00012	1.4478 ± 0.0028	0.8219 ± 0.0013
12	0.105987 ± 0.000073	1.5692 ± 0.0017	0.82085 ± 0.00084

Table 2 Continued

	Experiment = 4	Sample = 3	$a_W = 0.896226 \pm 0.000020$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1NaCl	2.91495 ± 0.00061	0.896236 ± 0.000031	1.04311 ± 0.00025
7NaCl	2.91546 ± 0.00061	0.896216 ± 0.000031	1.04314 ± 0.00025
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
2	0.47176 ± 0.00027	1.4115 ± 0.0012	0.92242 ± 0.00069
3	0.42226 ± 0.00024	1.4994 ± 0.0011	0.92016 ± 0.00065
4	0.35788 ± 0.00021	1.61495 ± 0.00093	0.91673 ± 0.00059
5	0.27879 ± 0.00016	1.75830 ± 0.00076	0.91198 ± 0.00054
6	0.163328 ± 0.000095	1.96880 ± 0.00060	0.90463 ± 0.00049
8	0.32833 ± 0.00022	1.6524 ± 0.0051	0.9216 ± 0.0022
9	0.29576 ± 0.00020	1.7129 ± 0.0046	0.9190 ± 0.0020
10	0.26679 ± 0.00018	1.7669 ± 0.0041	0.9167 ± 0.0018
11	0.22595 ± 0.00015	1.8439 ± 0.0035	0.9130 ± 0.0015
12	0.135978 ± 0.000093	2.0132 ± 0.0021	0.90511 ± 0.00097
	Experiment = 4	Sample = 4	$a_W = 0.828999 \pm 0.000029$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1NaCl	4.51158 ± 0.00095	0.828811 ± 0.000049	1.15511 ± 0.00027
7NaCl	4.50315 ± 0.00095	0.829186 ± 0.000049	1.15448 ± 0.00027
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
2	0.65178 ± 0.00038	1.9502 ± 0.0017	1.1428 ± 0.0010
3	0.58616 ± 0.00034	2.0814 ± 0.0015	1.13462 ± 0.00099
4	0.50038 ± 0.00029	2.2580 ± 0.0013	1.12229 ± 0.00093
5	0.39287 ± 0.00023	2.4778 ± 0.0011	1.10772 ± 0.00087
6	0.23271 ± 0.00013	2.80513 ± 0.00086	1.08678 ± 0.00081
8	0.45970 ± 0.00031	2.3136 ± 0.0071	1.1267 ± 0.0027
9	0.41557 ± 0.00028	2.4068 ± 0.0064	1.1196 ± 0.0025
10	0.37613 ± 0.00026	2.4910 ± 0.0058	1.1129 ± 0.0022
11	0.32005 ± 0.00022	2.6119 ± 0.0050	1.1032 ± 0.0019
12	0.19475 ± 0.00013	2.8833 ± 0.0031	1.0817 ± 0.0013
	Experiment = 4	Sample = 5	$a_W = 0.827524 \pm 0.000029$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1NaCl	4.54153 ± 0.00095	0.827478 ± 0.000050	1.15733 ± 0.00027
7NaCl	4.53947 ± 0.00095	0.827570 ± 0.000050	1.15717 ± 0.00027
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
2	0.65563 ± 0.00038	1.9617 ± 0.0017	1.1469 ± 0.0010
3	0.58950 ± 0.00034	2.0933 ± 0.0015	1.13890 ± 0.00100
4	0.50300 ± 0.00029	2.2698 ± 0.0013	1.12704 ± 0.00094
5	0.39506 ± 0.00023	2.4916 ± 0.0011	1.11203 ± 0.00088
6	0.23440 ± 0.00014	2.82552 ± 0.00086	1.08918 ± 0.00082
8	0.46248 ± 0.00032	2.3275 ± 0.0072	1.1306 ± 0.0027
9	0.41805 ± 0.00029	2.4212 ± 0.0065	1.1235 ± 0.0025
10	0.37842 ± 0.00026	2.5062 ± 0.0059	1.1167 ± 0.0022
11	0.32186 ± 0.00022	2.6266 ± 0.0050	1.1075 ± 0.0019
12	0.19576 ± 0.00013	2.8983 ± 0.0031	1.0864 ± 0.0013

Table 2 Continued

	Experiment = 4	Sample = 7	$a_W = 0.782564 \pm 0.000033$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1NaCl	5.5228 ± 0.0012	0.782588 ± 0.000060	1.23200 ± 0.00029
7NaCl	5.5239 ± 0.0012	0.782540 ± 0.000060	1.23208 ± 0.00029
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
2	0.76169 ± 0.00044	2.2790 ± 0.0019	1.2785 ± 0.0013
3	0.68590 ± 0.00040	2.4356 ± 0.0018	1.2677 ± 0.0013
4	0.58642 ± 0.00034	2.6462 ± 0.0015	1.2520 ± 0.0012
5	0.46191 ± 0.00027	2.9133 ± 0.0013	1.2317 ± 0.0011
6	0.27539 ± 0.00016	3.3196 ± 0.0010	1.2006 ± 0.0011
8	0.53980 ± 0.00037	2.7167 ± 0.0084	1.2545 ± 0.0031
9	0.48847 ± 0.00033	2.8290 ± 0.0076	1.2453 ± 0.0028
10	0.44249 ± 0.00030	2.9306 ± 0.0069	1.2368 ± 0.0025
11	0.37705 ± 0.00026	3.0771 ± 0.0059	1.2243 ± 0.0022
12	0.23020 ± 0.00016	3.4082 ± 0.0036	1.1964 ± 0.0015
	Experiment = 4	Sample = 8	$a_W = 0.802152 \pm 0.000032$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1NaCl	5.1007 ± 0.0011	0.802173 ± 0.000056	1.19945 ± 0.00028
7NaCl	5.1016 ± 0.0011	0.802130 ± 0.000056	1.19952 ± 0.00028
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
2	0.71633 ± 0.00041	2.1433 ± 0.0018	1.2224 ± 0.0012
3	0.64475 ± 0.00037	2.2895 ± 0.0017	1.2126 ± 0.0011
4	0.55074 ± 0.00032	2.4853 ± 0.0014	1.1987 ± 0.0011
5	0.43334 ± 0.00025	2.7331 ± 0.0012	1.1806 ± 0.0010
6	0.25796 ± 0.00015	3.10950 ± 0.00095	1.15250 ± 0.00096
8	0.50675 ± 0.00035	2.5504 ± 0.0079	1.2016 ± 0.0029
9	0.45841 ± 0.00031	2.6549 ± 0.0071	1.1931 ± 0.0027
10	0.41511 ± 0.00028	2.7492 ± 0.0064	1.1855 ± 0.0024
11	0.35352 ± 0.00024	2.8850 ± 0.0055	1.1741 ± 0.0021
12	0.21555 ± 0.00015	3.1912 ± 0.0034	1.1489 ± 0.0014
	Experiment = 6	Sample = 1	$a_W = 0.923548 \pm 0.000039$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1H_2SO_4	1.79856 ± 0.00052	0.923514 ± 0.000060	0.81859 ± 0.00062
7H_2SO_4	1.79729 ± 0.00052	0.923582 ± 0.000060	0.81842 ± 0.00062
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
2	0.38728 ± 0.00022	1.15875 ± 0.00099	0.81565 ± 0.00067
3	0.126619 ± 0.000073	1.58714 ± 0.00048	0.81839 ± 0.00052
4	0.22132 ± 0.00013	1.43054 ± 0.00061	0.81783 ± 0.00055
5	0.29114 ± 0.00017	1.31536 ± 0.00076	0.81729 ± 0.00060
6	0.34291 ± 0.00020	1.23054 ± 0.00088	0.81663 ± 0.00063
8	0.26543 ± 0.00018	1.3358 ± 0.0041	0.8276 ± 0.0020
9	0.24211 ± 0.00017	1.3777 ± 0.0038	0.8262 ± 0.0018
10	0.21216 ± 0.00015	1.4302 ± 0.0033	0.8250 ± 0.0016
11	0.17281 ± 0.00012	1.4991 ± 0.0027	0.8235 ± 0.0013
12	0.107940 ± 0.000074	1.6151 ± 0.0017	0.81983 ± 0.00091

Table 2 Continued

	Experiment = 6	Sample = 2	a_W = 0.906008 ± 0.000044
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1H_2SO_4	2.11688 ± 0.00062	0.906009 ± 0.000069	0.86278 ± 0.00061
7H_2SO_4	2.11691 ± 0.00062	0.906007 ± 0.000069	0.86278 ± 0.00061
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
2	0.44542 ± 0.00026	1.3327 ± 0.0011	0.88017 ± 0.00075
3	0.147868 ± 0.000086	1.85350 ± 0.00056	0.86974 ± 0.00059
4	0.25699 ± 0.00015	1.66106 ± 0.00071	0.87415 ± 0.00062
5	0.33674 ± 0.00019	1.52135 ± 0.00087	0.87700 ± 0.00067
6	0.39551 ± 0.00023	1.4193 ± 0.0010	0.87872 ± 0.00071
8	0.30755 ± 0.00021	1.5478 ± 0.0048	0.8864 ± 0.0021
9	0.28091 ± 0.00019	1.5984 ± 0.0044	0.8838 ± 0.0019
10	0.24655 ± 0.00017	1.6620 ± 0.0038	0.8811 ± 0.0017
11	0.20129 ± 0.00014	1.7461 ± 0.0031	0.8774 ± 0.0014
12	0.126224 ± 0.000086	1.8887 ± 0.0020	0.87009 ± 0.00099
	Experiment = 6	Sample = 3	a_W = 0.890157 ± 0.000048
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1H_2SO_4	2.38794 ± 0.00070	0.890156 ± 0.000076	0.90162 ± 0.00061
7H_2SO_4	2.38792 ± 0.00070	0.890158 ± 0.000076	0.90162 ± 0.00061
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
2	0.49371 ± 0.00029	1.4772 ± 0.0013	0.93606 ± 0.00082
3	0.165765 ± 0.000096	2.07783 ± 0.00063	0.91457 ± 0.00065
4	0.28683 ± 0.00017	1.85397 ± 0.00079	0.92323 ± 0.00069
5	0.37471 ± 0.00022	1.69290 ± 0.00097	0.92906 ± 0.00074
6	0.43913 ± 0.00025	1.5758 ± 0.0011	0.93296 ± 0.00078
8	0.34250 ± 0.00023	1.7237 ± 0.0053	0.9383 ± 0.0023
9	0.31315 ± 0.00021	1.7819 ± 0.0049	0.9346 ± 0.0021
10	0.27520 ± 0.00019	1.8551 ± 0.0043	0.9305 ± 0.0018
11	0.22510 ± 0.00015	1.9526 ± 0.0035	0.9249 ± 0.0015
12	0.141581 ± 0.000097	2.1185 ± 0.0022	0.9144 ± 0.0011
	Experiment = 6	Sample = 4	a_W = 0.880357 ± 0.000050
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1H_2SO_4	2.54885 ± 0.00074	0.880350 ± 0.000081	0.92512 ± 0.00061
7H_2SO_4	2.54862 ± 0.00074	0.880364 ± 0.000081	0.92509 ± 0.00061
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
2	0.52208 ± 0.00030	1.5621 ± 0.0013	0.96942 ± 0.00087
3	0.17633 ± 0.00010	2.21028 ± 0.00067	0.94157 ± 0.00069
4	0.30440 ± 0.00018	1.96750 ± 0.00084	0.95273 ± 0.00073
5	0.39705 ± 0.00023	1.7939 ± 0.0010	0.96019 ± 0.00078
6	0.46477 ± 0.00027	1.6678 ± 0.0012	0.96535 ± 0.00083
8	0.36308 ± 0.00025	1.8273 ± 0.0056	0.9693 ± 0.0023
9	0.33214 ± 0.00023	1.8899 ± 0.0051	0.9649 ± 0.0021
10	0.29208 ± 0.00020	1.9689 ± 0.0045	0.9601 ± 0.0019
11	0.23916 ± 0.00016	2.0746 ± 0.0037	0.9534 ± 0.0016
12	0.15068 ± 0.00010	2.2546 ± 0.0024	0.9410 ± 0.0011

Table 2 Continued

	Experiment = 6	Sample = 5	$a_W = 0.878879 \pm 0.000051$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1H_2SO_4	2.57263 ± 0.00075	0.878876 ± 0.000082	0.92862 ± 0.00061
7H_2SO_4	2.57253 ± 0.00075	0.878882 ± 0.000082	0.92860 ± 0.00061
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
2	0.52623 ± 0.00030	1.5745 ± 0.0013	0.97445 ± 0.00088
3	0.17788 ± 0.00010	2.22966 ± 0.00067	0.94569 ± 0.00070
4	0.30701 ± 0.00018	1.98442 ± 0.00084	0.95706 ± 0.00074
5	0.40034 ± 0.00023	1.8087 ± 0.0010	0.96485 ± 0.00079
6	0.46858 ± 0.00027	1.6815 ± 0.0012	0.97013 ± 0.00083
8	0.36611 ± 0.00025	1.8425 ± 0.0057	0.9740 ± 0.0024
9	0.33494 ± 0.00023	1.9059 ± 0.0052	0.9695 ± 0.0022
10	0.29460 ± 0.00020	1.9859 ± 0.0046	0.9645 ± 0.0019
11	0.24123 ± 0.00017	2.0926 ± 0.0037	0.9576 ± 0.0016
12	0.15203 ± 0.00010	2.2749 ± 0.0024	0.9449 ± 0.0011
	Experiment = 6	Sample = 6	$a_W = 0.855456 \pm 0.000055$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1H_2SO_4	2.93849 ± 0.00086	0.855431 ± 0.000092	0.98326 ± 0.00061
7H_2SO_4	2.93773 ± 0.00086	0.855481 ± 0.000092	0.98314 ± 0.00061
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
2	0.59008 ± 0.00034	1.7655 ± 0.0015	1.05084 ± 0.00100
3	0.20179 ± 0.00012	2.52941 ± 0.00076	1.00803 ± 0.00080
4	0.34664 ± 0.00020	2.24053 ± 0.00095	1.02501 ± 0.00085
5	0.45063 ± 0.00026	2.0359 ± 0.0012	1.03651 ± 0.00090
6	0.52630 ± 0.00030	1.8886 ± 0.0013	1.04445 ± 0.00095
8	0.41244 ± 0.00028	2.0757 ± 0.0064	1.0455 ± 0.0025
9	0.37774 ± 0.00026	2.1494 ± 0.0059	1.0395 ± 0.0023
10	0.33272 ± 0.00023	2.2429 ± 0.0052	1.0326 ± 0.0021
11	0.27299 ± 0.00019	2.3681 ± 0.0042	1.0233 ± 0.0017
12	0.17262 ± 0.00012	2.5830 ± 0.0027	1.0063 ± 0.0012
	Experiment = 6	Sample = 7	$a_W = 0.830569 \pm 0.000060$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1H_2SO_4	3.30503 ± 0.00096	0.83055 ± 0.00010	1.03945 ± 0.00062
7H_2SO_4	3.30455 ± 0.00096	0.83059 ± 0.00010	1.03937 ± 0.00062
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
2	0.65387 ± 0.00038	1.9564 ± 0.0017	1.1276 ± 0.0011
3	0.22565 ± 0.00013	2.82851 ± 0.00085	1.07191 ± 0.00092
4	0.38624 ± 0.00022	2.4965 ± 0.0011	1.09389 ± 0.00097
5	0.50089 ± 0.00029	2.2630 ± 0.0013	1.1089 ± 0.0010
6	0.58394 ± 0.00034	2.0955 ± 0.0015	1.1194 ± 0.0011
8	0.45867 ± 0.00031	2.3084 ± 0.0071	1.1179 ± 0.0027
9	0.42044 ± 0.00029	2.3923 ± 0.0065	1.1106 ± 0.0025
10	0.37070 ± 0.00025	2.4990 ± 0.0057	1.1021 ± 0.0022
11	0.30458 ± 0.00021	2.6422 ± 0.0047	1.0906 ± 0.0019
12	0.19319 ± 0.00013	2.8908 ± 0.0030	1.0692 ± 0.0013

Table 2 Continued

	Experiment = 6	Sample = 8	$a_W = 0.831856 \pm 0.000060$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1H_2SO_4	3.28677 ± 0.00096	0.83182 ± 0.00010	1.03661 ± 0.00062
7H_2SO_4	3.28584 ± 0.00096	0.83189 ± 0.00010	1.03647 ± 0.00062
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
2	0.65065 ± 0.00038	1.9468 ± 0.0017	1.1238 ± 0.0011
3	0.22452 ± 0.00013	2.81437 ± 0.00085	1.06831 ± 0.00091
4	0.38434 ± 0.00022	2.4842 ± 0.0011	1.09012 ± 0.00096
5	0.49843 ± 0.00029	2.2519 ± 0.0013	1.1051 ± 0.0010
6	0.58118 ± 0.00034	2.0856 ± 0.0015	1.1153 ± 0.0011
8	0.45628 ± 0.00031	2.2963 ± 0.0071	1.1144 ± 0.0027
9	0.41832 ± 0.00029	2.3803 ± 0.0065	1.1069 ± 0.0025
10	0.36881 ± 0.00025	2.4862 ± 0.0057	1.0985 ± 0.0022
11	0.30306 ± 0.00021	2.6289 ± 0.0047	1.0869 ± 0.0019
12	0.19219 ± 0.00013	2.8759 ± 0.0030	1.0658 ± 0.0013
	Experiment = 6	Sample = 9	$a_W = 0.835981 \pm 0.000059$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1H_2SO_4	3.22661 ± 0.00094	0.835987 ± 0.000100	1.02731 ± 0.00062
7H_2SO_4	3.22679 ± 0.00094	0.835975 ± 0.000100	1.02734 ± 0.00062
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
2	0.64016 ± 0.00037	1.9154 ± 0.0016	1.1115 ± 0.0011
3	0.22060 ± 0.00013	2.76518 ± 0.00083	1.05810 ± 0.00089
4	0.37790 ± 0.00022	2.4426 ± 0.0010	1.07890 ± 0.00094
5	0.49015 ± 0.00028	2.2145 ± 0.0013	1.09351 ± 0.00100
6	0.57171 ± 0.00033	2.0516 ± 0.0015	1.1033 ± 0.0010
9	0.41122 ± 0.00028	2.3399 ± 0.0064	1.0957 ± 0.0025
10	0.36257 ± 0.00025	2.4441 ± 0.0056	1.0874 ± 0.0022
11	0.29782 ± 0.00020	2.5835 ± 0.0046	1.0763 ± 0.0018
12	0.18843 ± 0.00013	2.8195 ± 0.0030	1.0579 ± 0.0013
	Experiment = 6	Sample = 10	$a_W = 0.813828 \pm 0.000063$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1H_2SO_4	3.5417 ± 0.0010	0.81381 ± 0.00011	1.07641 ± 0.00062
7H_2SO_4	3.5411 ± 0.0010	0.81385 ± 0.00011	1.07631 ± 0.00062
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
2	0.69527 ± 0.00040	2.0803 ± 0.0018	1.1768 ± 0.0012
3	0.24110 ± 0.00014	3.02213 ± 0.00091	1.11328 ± 0.00100
4	0.41190 ± 0.00024	2.6623 ± 0.0011	1.1383 ± 0.0011
5	0.53345 ± 0.00031	2.4101 ± 0.0014	1.1554 ± 0.0011
6	0.62145 ± 0.00036	2.2301 ± 0.0016	1.1672 ± 0.0012
9	0.44802 ± 0.00031	2.5493 ± 0.0069	1.1565 ± 0.0026
10	0.39522 ± 0.00027	2.6642 ± 0.0061	1.1471 ± 0.0023
11	0.32511 ± 0.00022	2.8203 ± 0.0051	1.1338 ± 0.0020
12	0.20609 ± 0.00014	3.0837 ± 0.0032	1.1122 ± 0.0014

Table 2 Continued

	Experiment = 6	Sample = 11	$a_W = 0.818207 \pm 0.000062$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
$1H_2SO_4$	3.4805 ± 0.0010	0.81818 ± 0.00011	1.06681 ± 0.00062
$7H_2SO_4$	3.4799 ± 0.0010	0.81823 ± 0.00011	1.06671 ± 0.00062
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
2	0.68425 ± 0.00040	2.0473 ± 0.0017	1.1646 ± 0.0012
3	0.23705 ± 0.00014	2.97137 ± 0.00090	1.10280 ± 0.00098
4	0.40507 ± 0.00023	2.6182 ± 0.0011	1.1273 ± 0.0010
5	0.52479 ± 0.00030	2.3709 ± 0.0014	1.1439 ± 0.0011
6	0.61150 ± 0.00035	2.1944 ± 0.0016	1.1553 ± 0.0011
9	0.44062 ± 0.00030	2.5072 ± 0.0068	1.1453 ± 0.0026
10	0.38871 ± 0.00027	2.6203 ± 0.0060	1.1360 ± 0.0023
11	0.31964 ± 0.00022	2.7728 ± 0.0050	1.1231 ± 0.0019
12	0.20257 ± 0.00014	3.0311 ± 0.0032	1.1020 ± 0.0014

[a]Value is the arithmetic mean of each of the individual a_W values calculated for the standards for each sample.
[b]Number designates the sample cup. Standard solute is identified by subscripted compound.
[c]Molality of solute in the standard solution at equilibrium.
[d]Molality of iron(III) sulfate in the test solution at equilibrium.
[e]Molality of sulfuric acid in the test solution at equilibrium.

certainties for temperature (± 0.01 K) and the degree of dissociation of sulfuric acid (α). The value of α is required in the calculation of the value ϕ_{Std} for the sulfuric acid standard solutions. The extended Pitzer model [17] utilized included tabulation of α to 0.0000x; thus, an uncertainty of ± 0.00003 was assigned to all values of α used to calculate ϕ_{Std} for the sulfuric acid standards.

The results are presented in Tables 2 and 3. These tables are arranged such that the results of each measurement (sample) are grouped. The heading for each block of data indicates the experiment number, the sample number and the value of a_w calculated for that particular equilibration. The value of a_w listed in the heading is the arithmetic mean of the individual values of a_w calculated for each of the standard solutions. The first values listed in each block of data are those for the standard solutions. The cup number of each standard is listed with a subscript indicating the identity of the standard solute; thus, the column labeled "[Std]" displays the concentration of the designated standard solute. The columns labeled a_w and ϕ_{Std} present the individual values for the activity of water and the stoichiometric osmotic coefficient, respectively, for the standard solutions in the designated cups. The lower portion of each block of data comprises the identification numbers for the test cups, the concentration of iron(III) sulfate and sulfuric acid in the test solution at equilibrium, and the value of ϕ_S calculated for the test solution (Tables 2 and 3).

Throughout the different experiments, the individual values of a_w varied from 0.98339 to 0.78274 at 298.15 K and from 0.96689 to 0.78519 at 323.15 K (Tables 2 and 3). The molal concentration of sodium chloride ranged from 0.50189 to 5.5239 mol·kg^{-1} in the 298.15 K experiments, whereas the range in the 323.15 K experiments was from 0.99144 to 5.4730 mol·kg^{-1} (Tables 2 and 3). Values of ϕ_{Std} for the sodium chloride solutions ranged from 0.92185 to 1.23081 at 298.15 K and from 0.94263 to 1.22695 at 323.15 K (Tables 2 and 3). On the other hand, the molal concentrations and values of ϕ_{Std} for the sulfuric acid standard solutions ranged from 0.46017 to 3.7546 mol·kg^{-1} and from 0.67285 to 1.1100, respectively,

Table 3 Results of isopiestic measurements at 323.15 K[a]

Cup	Experiment = 3 [Std]/(mol·kg^{-1})	Sample = 13 a_W	$a_W = 0.941748 \pm 0.000013$ ϕ_{Std}
1NaCl	1.70362 ± 0.00036	0.941591 ± 0.000017	0.98052 ± 0.00020
7NaCl	1.70351 ± 0.00036	0.941594 ± 0.000017	0.98051 ± 0.00020
2H_2SO_4	1.46390 ± 0.00043	0.941878 ± 0.000038	0.75686 ± 0.00045
8H_2SO_4	1.46280 ± 0.00043	0.941930 ± 0.000038	0.75674 ± 0.00045
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
3	0.33177 ± 0.00019	0.99267 ± 0.00085	0.72047 ± 0.00047
4	0.26340 ± 0.00015	1.08842 ± 0.00068	0.72906 ± 0.00041
5	0.21801 ± 0.00013	1.15165 ± 0.00058	0.73504 ± 0.00037
6	0.17300 ± 0.00010	1.21561 ± 0.00049	0.74044 ± 0.00033
9	0.22575 ± 0.00015	1.1361 ± 0.0035	0.7363 ± 0.0017
10	0.18105 ± 0.00012	1.1986 ± 0.0028	0.7422 ± 0.0014
11	0.16825 ± 0.00012	1.2175 ± 0.0026	0.7434 ± 0.0013
12	0.126324 ± 0.000087	1.2781 ± 0.0020	0.7481 ± 0.0010
	Experiment = 3	Sample = 14	$a_W = 0.9586033 \pm 0.0000098$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1NaCl	1.23205 ± 0.00026	0.958509 ± 0.000012	0.95463 ± 0.00019
7NaCl	1.23203 ± 0.00026	0.958510 ± 0.000012	0.95463 ± 0.00019
2H_2SO_4	1.09146 ± 0.00032	0.958678 ± 0.000028	0.71541 ± 0.00045
8H_2SO_4	1.09056 ± 0.00032	0.958717 ± 0.000028	0.71531 ± 0.00045
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
3	0.25496 ± 0.00015	0.76285 ± 0.00065	0.66014 ± 0.00042
4	0.20110 ± 0.00012	0.83099 ± 0.00052	0.67237 ± 0.00035
5	0.165774 ± 0.000096	0.87572 ± 0.00044	0.68063 ± 0.00032
6	0.131030 ± 0.000076	0.92071 ± 0.00037	0.68835 ± 0.00028
9	0.17179 ± 0.00012	0.8646 ± 0.0027	0.6813 ± 0.0016
10	0.137223 ± 0.000094	0.9085 ± 0.0021	0.6895 ± 0.0013
11	0.127333 ± 0.000087	0.9214 ± 0.0020	0.6917 ± 0.0012
12	0.095293 ± 0.000065	0.9641 ± 0.0015	0.69826 ± 0.00094
	Experiment = 3	Sample = 15	$a_W = 0.9669518 \pm 0.0000081$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1NaCl	0.99144 ± 0.00021	0.9668871 ± 0.0000093	0.94268 ± 0.00018
7NaCl	0.99150 ± 0.00021	0.9668850 ± 0.0000093	0.94269 ± 0.00018
2H_2SO_4	0.89340 ± 0.00026	0.967003 ± 0.000023	0.69493 ± 0.00044
8H_2SO_4	0.89271 ± 0.00026	0.967032 ± 0.000023	0.69486 ± 0.00044
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
3	0.21227 ± 0.00012	0.63514 ± 0.00054	0.63007 ± 0.00039
4	0.166777 ± 0.000097	0.68915 ± 0.00043	0.64428 ± 0.00033
5	0.137176 ± 0.000079	0.72465 ± 0.00036	0.65363 ± 0.00029
6	0.108199 ± 0.000063	0.76028 ± 0.00030	0.66243 ± 0.00026
9	0.142206 ± 0.000097	0.7157 ± 0.0022	0.6540 ± 0.0015
10	0.113353 ± 0.000078	0.7504 ± 0.0018	0.6633 ± 0.0013
11	0.105093 ± 0.000072	0.7605 ± 0.0016	0.6660 ± 0.0012
12	0.078504 ± 0.000054	0.7943 ± 0.0012	0.67354 ± 0.00090

Table 3 Continued

	Experiment = 3	Sample = 16	$a_W = 0.881712 \pm 0.000021$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1NaCl	3.25436 ± 0.00068	0.881298 ± 0.000034	1.07766 ± 0.00023
7NaCl	3.25411 ± 0.00068	0.881308 ± 0.000034	1.07765 ± 0.00023
2H_2SO_4	2.59029 ± 0.00076	0.882131 ± 0.000069	0.89588 ± 0.00049
8H_2SO_4	2.59065 ± 0.00076	0.882111 ± 0.000069	0.89592 ± 0.00049
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
3	0.54524 ± 0.00032	1.6314 ± 0.0014	0.92042 ± 0.00072
4	0.43863 ± 0.00025	1.8125 ± 0.0011	0.91918 ± 0.00064
5	0.36635 ± 0.00021	1.93528 ± 0.00097	0.91834 ± 0.00060
6	0.29377 ± 0.00017	2.06422 ± 0.00083	0.91547 ± 0.00056
9	0.37904 ± 0.00026	1.9076 ± 0.0059	0.9207 ± 0.0022
10	0.30675 ± 0.00021	2.0308 ± 0.0048	0.9197 ± 0.0018
11	0.28585 ± 0.00020	2.0685 ± 0.0044	0.9187 ± 0.0017
12	0.21680 ± 0.00015	2.1935 ± 0.0034	0.9151 ± 0.0013
	Experiment = 3	Sample = 17	$a_W = 0.835701 \pm 0.000025$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1NaCl	4.34750 ± 0.00091	0.834990 ± 0.000045	1.15129 ± 0.00025
7NaCl	4.34112 ± 0.00091	0.835268 ± 0.000045	1.15085 ± 0.00025
2H_2SO_4	3.33256 ± 0.00097	0.836141 ± 0.000091	0.99363 ± 0.00053
8H_2SO_4	3.32846 ± 0.00097	0.836407 ± 0.000091	0.99308 ± 0.00053
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
3	0.67969 ± 0.00039	2.0337 ± 0.0017	1.05282 ± 0.00094
4	0.54965 ± 0.00032	2.2712 ± 0.0014	1.04594 ± 0.00086
5	0.46079 ± 0.00027	2.4342 ± 0.0012	1.04109 ± 0.00081
6	0.37066 ± 0.00021	2.6045 ± 0.0010	1.03459 ± 0.00078
9	0.47644 ± 0.00033	2.3978 ± 0.0074	1.0445 ± 0.0025
10	0.38691 ± 0.00027	2.5615 ± 0.0060	1.0397 ± 0.0021
11	0.36118 ± 0.00025	2.6136 ± 0.0056	1.0368 ± 0.0019
12	0.27498 ± 0.00019	2.7821 ± 0.0043	1.0288 ± 0.0015
	Experiment = 3	Sample = 18	$a_W = 0.820182 \pm 0.000026$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1NaCl	4.70188 ± 0.00099	0.819433 ± 0.000049	1.17553 ± 0.00025
7NaCl	4.69810 ± 0.00099	0.819601 ± 0.000049	1.17527 ± 0.00025
2H_2SO_4	3.5656 ± 0.0010	0.820795 ± 0.000098	1.02481 ± 0.00054
8H_2SO_4	3.5641 ± 0.0010	0.820898 ± 0.000098	1.02460 ± 0.00054
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
3	0.72149 ± 0.00042	2.1587 ± 0.0018	1.0957 ± 0.0010
4	0.58427 ± 0.00034	2.4143 ± 0.0015	1.08703 ± 0.00094
5	0.49013 ± 0.00028	2.5892 ± 0.0013	1.08128 ± 0.00089
6	0.39491 ± 0.00023	2.7749 ± 0.0011	1.07276 ± 0.00086
9	0.50683 ± 0.00035	2.5507 ± 0.0079	1.0847 ± 0.0026
10	0.41206 ± 0.00028	2.7280 ± 0.0064	1.0785 ± 0.0022
11	0.38465 ± 0.00026	2.7834 ± 0.0060	1.0754 ± 0.0020
12	0.29322 ± 0.00020	2.9666 ± 0.0046	1.0659 ± 0.0016

Table 3 Continued

	Experiment = 4	Sample = 9	$a_W = 0.858006 \pm 0.000024$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1NaCl	3.81165 ± 0.00080	0.858033 ± 0.000040	1.11491 ± 0.00024
7NaCl	3.81290 ± 0.00080	0.857980 ± 0.000040	1.11500 ± 0.00024
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
2	0.61129 ± 0.00035	1.8290 ± 0.0016	0.99504 ± 0.00083
3	0.54729 ± 0.00032	1.9434 ± 0.0014	0.99235 ± 0.00078
4	0.46399 ± 0.00027	2.0938 ± 0.0012	0.98835 ± 0.00073
5	0.36174 ± 0.00021	2.28151 ± 0.00099	0.98241 ± 0.00068
6	0.21245 ± 0.00012	2.56089 ± 0.00078	0.97211 ± 0.00063
8	0.42616 ± 0.00029	2.1448 ± 0.0066	0.9925 ± 0.0024
9	0.38396 ± 0.00026	2.2238 ± 0.0060	0.9895 ± 0.0021
10	0.34644 ± 0.00024	2.2944 ± 0.0054	0.9867 ±0.0019
11	0.29364 ± 0.00020	2.3964 ± 0.0046	0.9820 ± 0.0017
12	0.17707 ± 0.00012	2.6215 ± 0.0028	0.9716 ± 0.0011
	Experiment = 4	Sample = 10	$a_W = 0.842568 \pm 0.000026$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1NaCl	4.17199 ± 0.00088	0.842604 ± 0.000044	1.13933 ± 0.00025
7NaCl	4.17368 ± 0.00088	0.842531 ± 0.000044	1.13944 ± 0.00025
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
2	0.65415 ± 0.00038	1.9573 ± 0.0017	1.04007 ± 0.00091
3	0.58593 ± 0.00034	2.0806 ± 0.0015	1.03680 ± 0.00086
4	0.49717 ± 0.00029	2.2435 ± 0.0013	1.03174 ± 0.00081
5	0.38808 ± 0.00022	2.4476 ± 0.0011	1.02431 ± 0.00076
6	0.22895 ± 0.00013	2.75982 ± 0.00084	1.00899 ± 0.00071
8	0.45780 ± 0.00031	2.3040 ± 0.0071	1.0335 ± 0.0025
9	0.41224 ± 0.00028	2.3875 ± 0.0064	1.0309 ± 0.0022
10	0.37212 ± 0.00025	2.4645 ± 0.0058	1.0275 ± 0.0020
11	0.31566 ± 0.00022	2.5760 ± 0.0049	1.0218 ± 0.0017
12	0.19072 ± 0.00013	2.8237 ± 0.0030	1.0089 ± 0.0012
	Experiment = 4	Sample = 11	$a_W = 0.784904 \pm 0.000032$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1NaCl	5.4711 ± 0.0011	0.784946 ± 0.000057	1.22837 ± 0.00026
7NaCl	5.4730 ± 0.0011	0.784861 ± 0.000057	1.22850 ± 0.00026
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
2	0.80606 ± 0.00047	2.4118 ± 0.0021	1.1934 ± 0.0012
3	0.72359 ± 0.00042	2.5694 ± 0.0019	1.1870 ± 0.0012
4	0.61527 ± 0.00036	2.7764 ± 0.0016	1.1787 ± 0.0011
5	0.48209 ± 0.00028	3.0405 ± 0.0013	1.1658 ± 0.0011
6	0.28575 ± 0.00017	3.4445 ± 0.0011	1.1430 ± 0.0010
8	0.56724 ± 0.00039	2.8548 ± 0.0088	1.1793 ± 0.0029
9	0.51190 ± 0.00035	2.9647 ± 0.0079	1.1738 ± 0.0026
10	0.46273 ± 0.00032	3.0646 ± 0.0072	1.1683 ± 0.0024
11	0.39334 ± 0.00027	3.2100 ± 0.0061	1.1593 ± 0.0021
12	0.23884 ± 0.00016	3.5361 ± 0.0038	1.1391 ± 0.0014

Table 3 Continued

	Experiment = 4	Sample = 12	$a_W = 0.839319 \pm 0.000026$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1NaCl	4.24766 ± 0.00089	0.839329 ± 0.000044	1.14448 ± 0.00025
7NaCl	4.24811 ± 0.00089	0.839310 ± 0.000044	1.14451 ± 0.00025
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
2	0.66282 ± 0.00038	1.9832 ± 0.0017	1.04962 ± 0.00092
3	0.59391 ± 0.00034	2.1089 ± 0.0015	1.04593 ± 0.00088
4	0.50366 ± 0.00029	2.2728 ± 0.0013	1.04142 ± 0.00083
5	0.39340 ± 0.00023	2.4812 ± 0.0011	1.03325 ± 0.00077
6	0.23191 ± 0.00013	2.79548 ± 0.00085	1.01858 ± 0.00072
8	0.46369 ± 0.00032	2.3336 ± 0.0072	1.0434 ± 0.0025
9	0.41781 ± 0.00029	2.4198 ± 0.0065	1.0401 ± 0.0023
10	0.37723 ± 0.00026	2.4983 ± 0.0059	1.0365 ± 0.0021
11	0.32003 ± 0.00022	2.6117 ± 0.0050	1.0305 ± 0.0018
12	0.19351 ± 0.00013	2.8650 ± 0.0030	1.0168 ± 0.0012
	Experiment = 4	Sample = 13	$a_W = 0.837492 \pm 0.000027$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1NaCl	4.28943 ± 0.00090	0.837516 ± 0.000045	1.14733 ± 0.00025
7NaCl	4.29052 ± 0.00090	0.837469 ± 0.000045	1.14740 ± 0.00025
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
2	0.66756 ± 0.00039	1.9974 ± 0.0017	1.05414 ± 0.00093
3	0.59827 ± 0.00035	2.1244 ± 0.0015	1.05122 ± 0.00089
4	0.50718 ± 0.00029	2.2887 ± 0.0013	1.04705 ± 0.00084
5	0.39627 ± 0.00023	2.4993 ± 0.0011	1.03851 ± 0.00078
6	0.23378 ± 0.00014	2.81810 ± 0.00086	1.02298 ± 0.00073
8	0.46720 ± 0.00032	2.3513 ± 0.0072	1.0484 ± 0.0025
9	0.42088 ± 0.00029	2.4376 ± 0.0065	1.0454 ± 0.0023
10	0.38013 ± 0.00026	2.5175 ± 0.0059	1.0414 ± 0.0021
11	0.32247 ± 0.00022	2.6316 ± 0.0050	1.0355 ± 0.0018
12	0.19508 ± 0.00013	2.8882 ± 0.0031	1.0212 ± 0.0012
	Experiment = 4	Sample = 14	$a_W = 0.829803 \pm 0.000027$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1NaCl	4.46606 ± 0.00094	0.829812 ± 0.000047	1.15938 ± 0.00025
7NaCl	4.46647 ± 0.00094	0.829794 ± 0.000047	1.15941 ± 0.00025
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
2	0.68854 ± 0.00040	2.0601 ± 0.0018	1.07620 ± 0.00097
3	0.61726 ± 0.00036	2.1918 ± 0.0016	1.07188 ± 0.00093
4	0.52345 ± 0.00030	2.3621 ± 0.0014	1.06728 ± 0.00087
5	0.40931 ± 0.00024	2.5815 ± 0.0011	1.05773 ± 0.00082
6	0.24171 ± 0.00014	2.91360 ± 0.00089	1.04091 ± 0.00077
8	0.48229 ± 0.00033	2.4272 ± 0.0075	1.0684 ± 0.0026
9	0.43465 ± 0.00030	2.5173 ± 0.0067	1.0649 ± 0.0023
10	0.39266 ± 0.00027	2.6005 ± 0.0061	1.0606 ± 0.0021
11	0.33323 ± 0.00023	2.7194 ± 0.0052	1.0542 ± 0.0018
12	0.20177 ± 0.00014	2.9873 ± 0.0032	1.0387 ± 0.0012

Table 3 Continued

	Experiment = 4	Sample = 15	$a_W = 0.850958 \pm 0.000025$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1NaCl	3.98369 ± 0.00084	0.850702 ± 0.000042	1.12654 ± 0.00025
7NaCl	3.97170 ± 0.00083	0.851215 ± 0.000041	1.12573 ± 0.00024
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
2	0.62936 ± 0.00036	1.8831 ± 0.0016	1.01852 ± 0.00087
3	0.56396 ± 0.00033	2.0026 ± 0.0014	1.01488 ± 0.00082
4	0.47732 ± 0.00028	2.1539 ± 0.0012	1.01248 ± 0.00077
5	0.37251 ± 0.00022	2.3494 ± 0.0010	1.00539 ± 0.00072
6	0.21931 ± 0.00013	2.64367 ± 0.00081	0.99239 ± 0.00067
8	0.43995 ± 0.00030	2.2141 ± 0.0068	1.0132 ± 0.0024
9	0.39595 ± 0.00027	2.2932 ± 0.0061	1.0112 ± 0.0022
10	0.35752 ± 0.00024	2.3678 ± 0.0055	1.0076 ± 0.0020
11	0.30327 ± 0.00021	2.4749 ± 0.0047	1.0020 ± 0.0017
12	0.18318 ± 0.00013	2.7120 ± 0.0029	0.9897 ± 0.0011
	Experiment = 4	Sample = 16	$a_W = 0.908060 \pm 0.000017$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1NaCl	2.58764 ± 0.00054	0.908070 ± 0.000026	1.03435 ± 0.00022
7NaCl	2.58815 ± 0.00054	0.908050 ± 0.000026	1.03438 ± 0.00022
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
2	0.45443 ± 0.00026	1.3597 ± 0.0012	0.84295 ± 0.00061
3	0.40518 ± 0.00023	1.4388 ± 0.0010	0.84413 ± 0.00056
4	0.34087 ± 0.00020	1.53821 ± 0.00088	0.84724 ± 0.00052
5	0.26397 ± 0.00015	1.66488 ± 0.00072	0.84784 ± 0.00047
6	0.153641 ± 0.000089	1.85203 ± 0.00056	0.84652 ± 0.00042
8	0.31336 ± 0.00021	1.5770 ± 0.0049	0.8501 ± 0.0020
9	0.28111 ± 0.00019	1.6281 ± 0.0044	0.8511 ± 0.0018
10	0.25304 ± 0.00017	1.6758 ± 0.0039	0.8508 ± 0.0016
11	0.21359 ± 0.00015	1.7431 ± 0.0033	0.8502 ± 0.0014
12	0.127780 ± 0.000088	1.8918 ± 0.0020	0.84786 ± 0.00089
	Experiment = 4	Sample = 17	$a_W = 0.854905 \pm 0.000025$
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1NaCl	3.88396 ± 0.00082	0.854960 ± 0.000041	1.11980 ± 0.00024
7NaCl	3.88652 ± 0.00082	0.854850 ± 0.000041	1.11997 ± 0.00024
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
2	0.61793 ± 0.00036	1.8489 ± 0.0016	1.00760 ± 0.00085
3	0.55332 ± 0.00032	1.9648 ± 0.0014	1.00474 ± 0.00080
4	0.46835 ± 0.00027	2.1135 ± 0.0012	1.00229 ± 0.00075
5	0.36514 ± 0.00021	2.30294 ± 0.00100	0.99628 ± 0.00070
6	0.21524 ± 0.00012	2.59457 ± 0.00079	0.98218 ± 0.00065
8	0.43183 ± 0.00030	2.1733 ± 0.0067	1.0027 ± 0.0024
9	0.38831 ± 0.00027	2.2489 ± 0.0060	1.0016 ± 0.0022
10	0.35068 ± 0.00024	2.3225 ± 0.0054	0.9978 ± 0.0020
11	0.29710 ± 0.00020	2.4246 ± 0.0046	0.9935 ± 0.0017
12	0.17942 ± 0.00012	2.6564 ± 0.0028	0.9815 ± 0.0011

Table 3 Continued

	Experiment = 4	Sample = 18	a_W = 0.944082 ± 0.000011
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1NaCl	1.63508 ± 0.00034	0.944091 ± 0.000016	0.97660 ± 0.00020
7NaCl	1.63558 ± 0.00034	0.944073 ± 0.000016	0.97663 ± 0.00020
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
2	0.31762 ± 0.00018	0.95033 ± 0.00081	0.71956 ± 0.00047
3	0.28168 ± 0.00016	1.00021 ± 0.00072	0.72447 ± 0.00043
4	0.23519 ± 0.00014	1.06129 ± 0.00061	0.73264 ± 0.00039
5	0.18046 ± 0.00010	1.13816 ± 0.00049	0.73994 ± 0.00034
6	0.104054 ± 0.000060	1.25430 ± 0.00038	0.74575 ± 0.00029
8	0.21606 ± 0.00015	1.0874 ± 0.0033	0.7356 ± 0.0017
9	0.19280 ± 0.00013	1.1166 ± 0.0030	0.7404 ± 0.0016
10	0.17307 ± 0.00012	1.1462 ± 0.0027	0.7421 ± 0.0014
11	0.145382 ± 0.000100	1.1864 ± 0.0023	0.7452 ± 0.0012
12	0.086193 ± 0.000059	1.2761 ± 0.0014	0.74993 ± 0.00075
	Experiment = 4	Sample = 19	a_W = 0.9489939 ± 0.0000098
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1NaCl	1.49967 ± 0.00032	0.948990 ± 0.000015	0.96900 ± 0.00020
7NaCl	1.49944 ± 0.00032	0.948998 ± 0.000015	0.96898 ± 0.00020
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/ (mol·kg^{-1})	ϕ_s
2	0.29635 ± 0.00017	0.88671 ± 0.00076	0.70164 ± 0.00045
3	0.26264 ± 0.00015	0.93262 ± 0.00067	0.70690 ± 0.00041
4	0.21926 ± 0.00013	0.98942 ± 0.00057	0.71499 ± 0.00037
5	0.167983 ± 0.000097	1.05946 ± 0.00046	0.72322 ± 0.00032
6	0.096463 ± 0.000056	1.16279 ± 0.00035	0.73189 ± 0.00028
8	0.20093 ± 0.00014	1.0112 ± 0.0031	0.7196 ± 0.0017
9	0.17925 ± 0.00012	1.0381 ± 0.0028	0.7246 ± 0.0015
10	0.16085 ± 0.00011	1.0653 ± 0.0025	0.7265 ± 0.0014
11	0.135051 ± 0.000093	1.1021 ± 0.0021	0.7299 ± 0.0012
12	0.079965 ± 0.000055	1.1839 ± 0.0013	0.73544 ± 0.00073
	Experiment = 4	Sample = 20	a_W = 0.9566018 ± 0.0000083
Cup	[Std]/(mol·kg^{-1})	a_W	ϕ_{Std}
1NaCl	1.28611 ± 0.00027	0.956603 ± 0.000012	0.95746 ± 0.00019
7NaCl	1.28619 ± 0.00027	0.956600 ± 0.000012	0.95746 ± 0.00019
Cup	[$Fe_2(SO_4)_3$]/(mol·kg^{-1})	[H_2SO_4]/(mol·kg^{-1})	ϕ_s
2	0.26144 ± 0.00015	0.78225 ± 0.00067	0.67403 ± 0.00043
3	0.23132 ± 0.00013	0.82141 ± 0.00059	0.68020 ± 0.00039
4	0.19240 ± 0.00011	0.86822 ± 0.00050	0.69053 ± 0.00035
5	0.147134 ± 0.000085	0.92797 ± 0.00040	0.69976 ± 0.00030
6	0.084240 ± 0.000049	1.01546 ± 0.00031	0.71026 ± 0.00026
8	0.17654 ± 0.00012	0.8885 ± 0.0027	0.6941 ± 0.0016
9	0.15730 ± 0.00011	0.9110 ± 0.0024	0.6998 ± 0.0015
10	0.141005 ± 0.000097	0.9339 ± 0.0022	0.7024 ± 0.0013
11	0.118243 ± 0.000081	0.9650 ± 0.0018	0.7065 ± 0.0011
12	0.069811 ± 0.000048	1.0336 ± 0.0011	0.71392 ± 0.00071

[a] See the footnotes for Table 2.

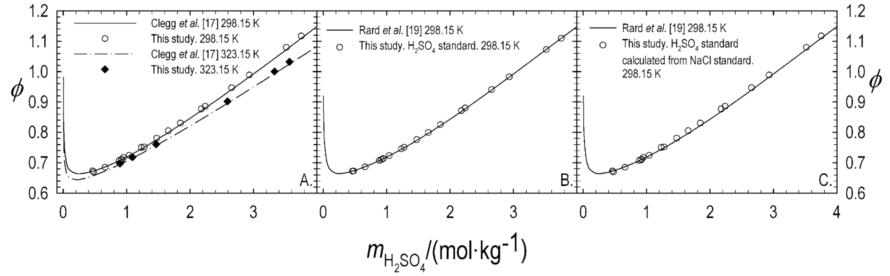

Fig. 1 A. Values of ϕ_S calculated for the sulfuric acid standard solutions using the values of ϕ_{Std} obtained from the NaCl standards in Experiments 1 to 3, compared with the extended-Pitzer model for sulfuric acid used in this study [17] at 298.15 and 323.15 K. B. Comparison of the values of ϕ_{Std} calculated for the sulfuric acid standards in Experiments 1 to 3 of this study compared with the model for sulfuric acid of Rard *et al.* [19] at 298.15 K. C. Comparison of values of ϕ_S calculated for the sulfuric acid standard solutions using the values of ϕ_{Std} obtained from the NaCl standards in Experiments 1 to 3 compared with the model for sulfuric acid of Rard *et al.* [19] at 298.15 K.

at 298.15 K and from 0.89271 to 3.5656 mol·kg^{-1}, and 0.69486 to 1.02460 respectively, at 323.15 K (Tables 2 and 3).

Values of ϕ_S were calculated for each test solution using each set of standards. One value of ϕ_S was calculated using the value of ϕ_{Std} obtained by averaging the individual ϕ_{Std} values calculated for the sodium chloride standard solutions whereas another was calculated using the average value of ϕ_{Std} obtained for the sulfuric acid standard solutions. When both sets of standards were available, these two different values of ϕ_S agreed to within 0.1% and were averaged to produce the test solution ϕ_S values reported in Tables 2 and 3.

The system achieved isopiestic equilibrium prior to each of five sampling episodes at 298.15 K during Experiment 1 as indicated by values of a_w that agreed to within 0.01% (Table 2). One of the cups containing the sulfuric acid standard solution ($x = 1.00000$) lost some solution on the last sampling episode and the experiment was terminated. The value of ϕ_S for the test solutions was, therefore, calculated using the arithmetic average of the values of ϕ_{Std} obtained from the sodium chloride standards only on that sampling event.

During Experiment 2, the system reached isopiestic equilibrium on four of the five sampling episodes. The system did not equilibrate prior to the first sampling episode, but the values of a_w agreed to within a 0.1% for the other four sampling episodes (Table 2). On the last sampling event, the cup filled with a test solution of $x = 0.83423$ lost its lid and no ϕ_S calculation for that particular test solution was performed.

Experiment 3 was conducted at 298.15 and 323.15 K. The system reached isopiestic equilibrium on eleven of the twelve sampling events at 298.15 K and on six of the seven at 323.15 K. The values of a_w for these standard solutions agreed to within 0.008% at 298.15 K (Table 2) and 0.01% at 323.15 K (Table 3). The system did not reach equilibrium in one of the sampling episodes at both temperatures due to the formation of a precipitate in one or more cups.

Experiment 4 was also conducted at 298.15 and 323.15 K. Isopiestic equilibrium was achieved by the system on seven of the eight sampling episodes at 298.15 K and for all the sampling events at 323.15 K. Sodium chloride was the only reference standard used in this experiment and the values of a_w for the standard solutions (Tables 2 and 3) are in good agreement with the greatest discrepancy being 0.01%. One sampling interval of this experiment did not reach equilibrium due to the formation of a precipitate in one of the

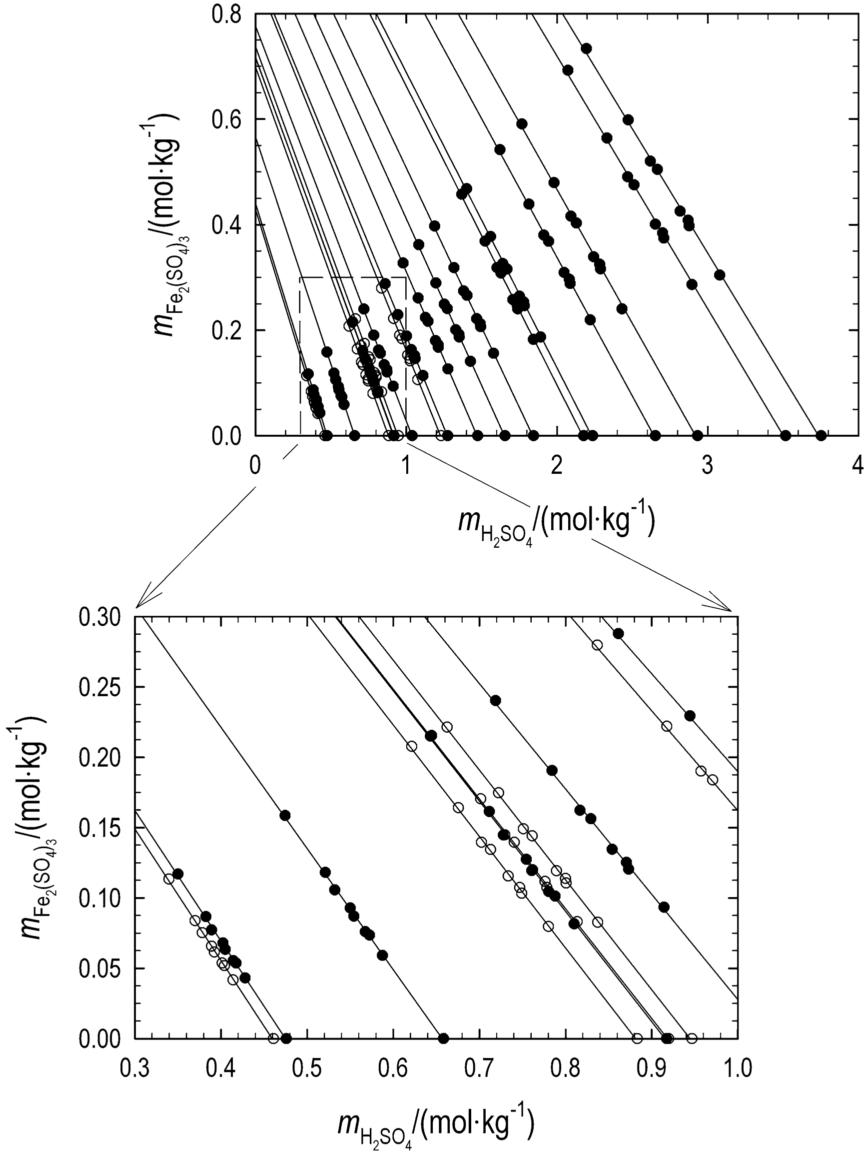

Fig. 2 Isopleths of a_W for $Fe_2(SO_4)_3$–H_2SO_4–H_2O solutions at 298.15 K calculated using the Zdanovskii rule. *Open circles* are used for clarity where isopleths are spaced closely

cups. As in Experiment 3, the addition of water allowed the system to reach equilibrium on subsequent sampling episodes.

Experiment 6 was performed at 298.15 K using sulfuric acid as the reference standard. In this experiment, the system reached isopiestic equilibrium prior to eleven sampling episodes with values of a_w agreeing to within 0.001%. The cup filled with a test solution, in which $x =$ 0.83423, lost solution on the ninth sampling episode and was not considered in subsequent sampling episodes.

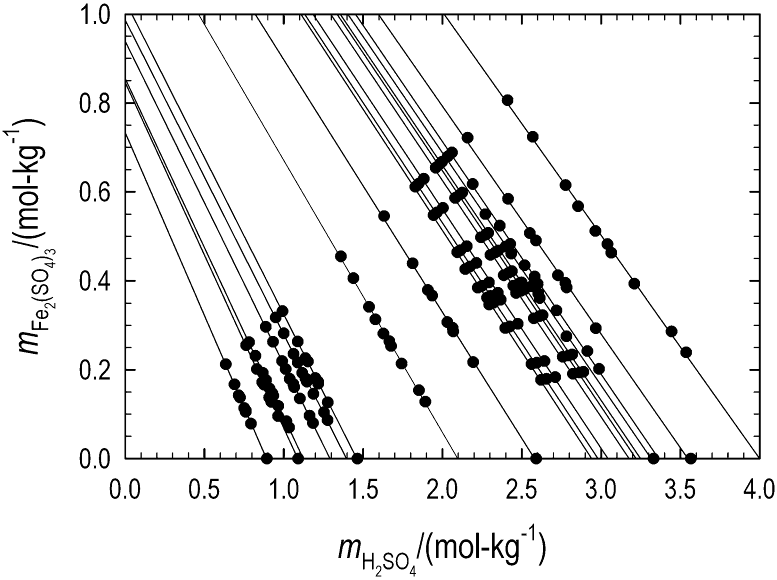

Fig. 3 Isopleths of a_W for $Fe_2(SO_4)_3$–H_2SO_4–H_2O solutions at 323.15 K calculated using the Zdanovskii rule

4 Discussion

Discussion of the data reported here will be brief. These data were collected as part of a larger effort to examine FeO–Fe_2O_3–SO_3–H_2O solutions. Measurements of the osmotic coefficients of iron(II) sulfate solutions are underway; those values will be combined with the data presented here to generate a comprehensive activity model for iron(II)—iron(III) sulfate solutions. It is, however, possible to assess the quality of the data presented here and to compare some of these results with experimental results published previously.

Experiments 1 to 3 utilized both NaCl and H_2SO_4 standard solutions so that the data can be assessed by comparing the results obtained for the H_2SO_4–H_2O reference solutions to the model published by Clegg *et al.* [17]. Figure 1A displays the value of ϕ_S of the sulfuric acid standard solutions in Experiments 1 to 3 as calculated using the ϕ_{Std} value calculated for the sodium chloride standard solutions only, plotted against the concentration of the sulfuric acid reference solutions. Also plotted on Fig. 1A is the relation between the value for the stoichiometric osmotic coefficient for aqueous sulfuric acid solutions and concentration that was used in this study [17]. These values are in excellent agreement at concentrations of sulfuric acid below 1.5 mol·kg^{-1} at temperatures of 298.15 K and 323.15 K. Although the two systems begin to deviate at higher sulfuric acid concentrations, the agreement is considered to be sufficiently close that either standard is suitable in these experiments. Recently published isopiestic measurements in the Fe_2O_3–SO_3–H_2O system [21] utilized sulfuric acid standard solutions but relied on a different model published by Rard *et al.* [19] for calculating the osmotic coefficient of these solutions. In order to compare the Clegg *et al.* [17] model with that of Rard *et al.* [19], the values of ϕ_{Std} calculated for the sulfuric acid standard solutions in this study are compared with the model of Rard *et al.* [19] (Fig. 1B). The agreement is good over the entire range of concentrations considered and indicates that the values obtained

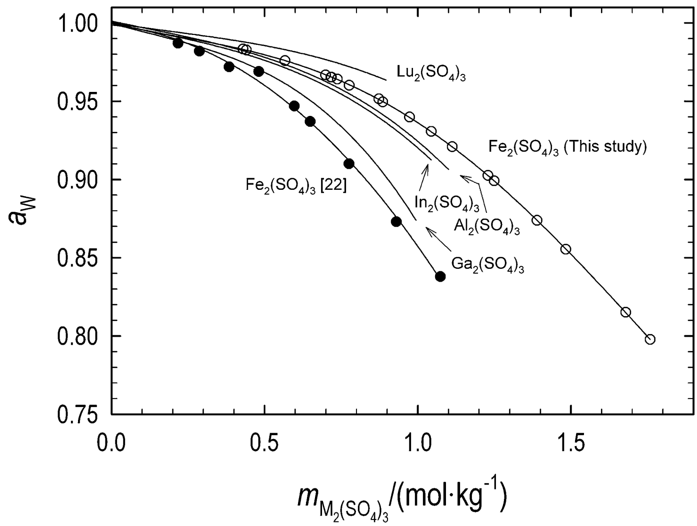

Fig. 4 Plot of values a_W calculated in this study compared with measurements of a_W in binary systems at 298.15 K comprising $Lu_2(SO_4)_3$–H_2O [31], $Al_2(SO_4)_3$–H_2O [32], $In_2(SO_4)_3$–H_2O [30], $Ga_2(SO_4)_3$–H_2O [29], and calculations of a_W for the $Fe_2(SO_4)_3$–H_2O binary system assuming Zdanovskii's rule linearity

here should be comparable to those obtained in the earlier effort [21]. Finally, the values of ϕ_S of the sulfuric acid standards in Experiments 1 to 3 calculated from the values of ϕ_{Std} for the sodium chloride standard solutions can be compared with the Rard *et al.* [19] model used in the recent publication [21]. The agreement is again excellent for those sulfuric acid concentrations less than 1.5 mol·kg^{-1} with slight deviations at higher concentrations (Fig. 1C).

These data generally follow the Zdanovskii rule [27] which demands that for any unique value of a_w,

$$\frac{m_{H_2SO_4}}{M_{H_2SO_4}} + \frac{m_{Fe_2(SO_4)_3}}{M_{Fe_2(SO_4)_3}} = 1 \tag{6}$$

where m_i denotes the molal concentration of component i in the solution, whereas M_i denotes the molal concentration of component i in an end-member solution that has the same activity of water as the mixture. The values obtained in this work can, therefore, be used to draw isopleths of a_w in concentration space (Figs. 2 and 3). Although for the Zdanovskii rule linearity holds only for solutes with the same charge types [28], the deviations from linear behavior observed in H_2O–H_2SO_4–$M_2(SO_4)_3$ systems are typically small [21, 22, 29, 30] and the concentrations of $Fe_2(SO_4)_3$ required to produce requisite values of a_w could be calculated using first-order equations regressed to the data in Figs. 2 and 3. This approach was taken by Majima and Awakura [22] in an earlier isopiestic study of solutions in this same system. In contrast, Rumyantsev *et al.* [21] extended experimental measurements in this system through regions of supersaturation and fitted the data to second-order equations.

The estimated values of a_w as a function of concentration in the $Fe_2(SO_4)_3$–H_2O binary system obtained in this study, assuming Zdanovskii rule linearity, differ significantly from those obtained by Majima and Awakura [22] (Fig. 4). Rumyantsev *et al.* [20] also reported

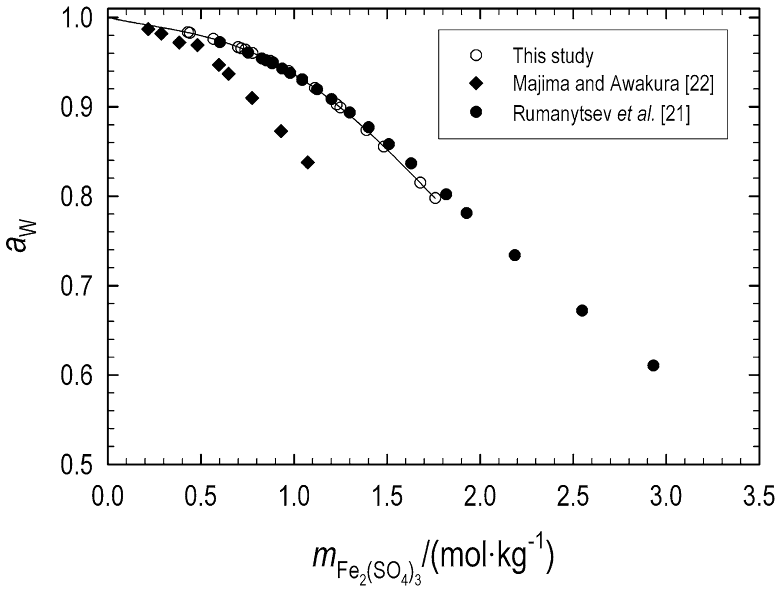

Fig. 5 Comparison of values of a_W for the $Fe_2(SO_4)_3$–H_2O binary system calculated in this study compared with those obtained by first-order regression of data published by Majima and Awakura [22] and Rumyantsev *et al.* [21]

a significant discrepancy between the calculated concentration of $Fe_2(SO_4)_3$ and a_w in the $Fe_2(SO_4)_3$–H_2O binary system as compared with the values presented by Majima and Awakura [22]. Whereas the values of a_w in aqueous $Fe_2(SO_4)_3$ solutions presented by Majima and Awakura decrease more rapidly with increasing solute concentration than do values of a_W in solutions of aqueous $Al_2(SO_4)_3$, $In_2(SO_4)_3$, $Ga_2(SO_4)_3$, or $Lu_2(SO_4)_3$, the estimates of a_w presented here are intermediate between those for aqueous $Al_2(SO_4)_3$ and $Lu_2(SO_4)_3$ solutions (Fig. 4). The values presented here are, however, in general agreement with those presented by Rumyantsev *et al.* [21] (Fig. 5). The values of a_w presented in Fig. 5 were obtained by regressing the Rumyantsev *et al.* data using a first-order equation (*viz*, assuming that the data followed the Zdanovskii rule linearity) and are not those presented in the original work. Those values [21] were collected over very wide ranges of xH_2SO_4 (0.9 to 0.04), the extrapolations to the $Fe_2(SO_4)_3$–H_2O binary system were short, and significant deviations between the first- and second-order extrapolations appear only at values of a_w less than 0.82. Significant differences between the values of a_w for the $Fe_2(SO_4)_3$–H_2O binary system calculated in this study and those obtained by first-order extrapolation of the Rumyantsev *et al.* data also appear only at the highest concentrations examined (Fig. 5). Although the values presented in Fig. 5 are useful in comparing and evaluating the three set of isopiestic values, they should not be considered to be accurate measures of the thermodynamic properties of pure aqueous $Fe_2(SO_4)_3$; the Zdanovskii rule linearity strictly holds only for solutes of similar charge types [28]. The approach is also likely to generate significant errors for the data collected at high concentrations as long extrapolations to the $Fe_2(SO_4)_3$–H_2O binary system are required for the data collected in this study. The comparison does confirm that the results of this study and those of Rumyantsev *et al.* [21] are in good general agreement.

5 Conclusions

This study reports the osmotic coefficients of $\{x\mathrm{H_2SO_4} + (1{-}x)\mathrm{Fe_2(SO_4)_3}\}$(aq) solutions at 298.15 and 323.15 K. In experiments that utilized NaCl and H_2SO_4 standards, the sets of standard solutions were in satisfactory agreement. The solutions approach Zdanovskii linearity and although values of a_w calculated for the $Fe_2(SO_4)_3$–H_2O binary at 298.15 K do not agree with all values published previously, they are in good agreement with the most comprehensive, recent study and are more similar to those published previously for other $M_2(SO_4)_3$–H_2O binary systems.

Acknowledgments Support for RMK and MVR was provided by US Geological Survey (1434-HQ-97–03191) and the National Science Foundation (EAR 0230323). DAP acknowledges financial support by the Division of Chemical Sciences, Geosciences and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.

References

1. Nordstrom, D.K., Alpers, C.N.: Geochemistry of acid mine waters. Rev. Econ. Geol. **6A**, 133–160 (1999)
2. Plumlee, G.S.: The environmental geology of mineral deposits. Rev. Econ. Geol. **6A**, 71–116 (1999)
3. Van Breeman, N.: Genesis, morphology and classification of acid sulfate soils in coastal plains. Soil Sci. Soc. Am. Spec. Pub. No. **10**, 95–108 (1982)
4. Joeckel, R.M., Ang Clement, B.J., VanFleet Bates, L.F.: Sulfate-mineral crusts from pyrite weathering and acid rock drainage in the Dakota Formation and Graneros Shale, Jefferson County, Nebraska. Chem. Geol. **215**, 433–452 (2005)
5. Rawlings D.E.: Biomining: Theory, Microbes & Industrial Processes. Springer-Verlag, Berlin (1997)
6. Nordstrom, D.K., Alpers, C.N., Ptacek, C.J., Blowes, D.W.: Negative pH and extremely acidic mine waters from Iron Mountain, California. Environ. Sci. Technol. **34**, 254–258 (2000)
7. Alpers, C.N., Nordstrom, D.K.: Geochemical evolution of extremely acid mine waters at Iron Mountain California-Are there any lower limits to pH? Proc. 2nd Intl. Conf. on the Abatement of Acidic Drainage CANMET, Ottawa, Canada **2**, 324–342 (1991)
8. Cathles L.M.: Attempts to model the industrial scale leaching of copper-bearing mine waste. Environmental Geochemistry of Sulfide Oxidation, ACS Symposium Series **550**, 123–131 (1994)
9. Platford, R.F.: Experimental methods: Isopiestic. Activity Coefficients in Electrolyte Solutions, CRC Press, Boca Eaton, FL, Vol. 1, 65–79 (1979)
10. Holmes, H.F, Mesmer, R.E.: Isopiestic studies of sulforic acid at elevated temperatures. Thermodynamic properties. J. Chem. Thermodyn. **24**, 317–328 (1992)
11. Clegg, S.L. Milioto, S., Palmer, D.A.: Osmotic and activity coefficients of aqueous $(NH_4)_2SO_4$ as a function of temperature, and aqueous $(NH_4)_2SO_4$–H_2SO_4 mixtures at 298.15 and 323.15 K. J. Chem. Eng. Data **41**, 455–467 (1996)
12. Archer, D.G.: Thermodynamic properties of the sodium chloride + water system. II. Thermodynamic properties of NaCl(aq), $\mathrm{NaCl{\cdot}2H_2O}$(cr), and phase equilibria. J. Phys. Chem. Ref. Data **21**, 793–829 (1992)
13. Krumgalz, B.S., Pogorelsky, R., Pitzer, K.S.: Volumetric properties of single aqueous electrolytes from zero to saturation concentration at 298.15 K represented by Pitzer's ion-interaction equations. J. Phys. Chem. Ref. Data **25**, 663–689 (1996)
14. Pitzer, K.S., Peiper, J.C., Busey R.H.: Thermodynamic properties of aqueous sodium chloride solutions. J. Phys. Chem. Ref. Data **13**, 1–102 (1984)
15. Rogers, P.S.Z., Pitzer, K.S.: Volumetric properties of aqueous sodium chloride solutions. J. Phys. Chem. Ref. Data **11**, 15–81 (1982)
16. Silvester, L.F., Pitzer, K.S.: Thermodynamics of electrolytes. 8. High-temperature properties, including enthalpy and heat capacity, with application to sodium chloride. J. Phys. Chem. **81**, 1822–1828 (1977)
17. Clegg, S.L., Rard, J.A., Pitzer, K.S.: Thermodynamic properties of 0–6 $\mathrm{mol{\cdot}kg^{-1}}$ aqueous sulfuric acid from 273.15 to 328.15 K. J. Chem. Soc. Faraday Trans. **90**, 1875–1894 (1994)
18. Pitzer, K.S., Roy, R.N., Silvester, L.F.: Thermodynamics of electrolytes. 7. Sulfuric acid. J. Am. Chem. Soc. **99**, 4930–4936 (1977)

19. Rard, J.A., Habenschuss, A., Spedding, F.H.: A review of the osmotic coefficients of aqueous sulfuric acid at 25°C. J. Chem. Eng. Data **21**, 374–379 (1976)
20. Staples, B.R.: Activity and osmotic coefficients of aqueous sulfuric acid at 298.15 K. J. Phys. Chem. Ref. Data **10**, 779–798 (1981)
21. Rumyantsev, A., Hageman, S., Moog, H.C.: Isopiestic investigation of the systems $Fe_2(SO_4)_3$–H_2SO_4–H_2O, $FeCl_3$–H_2O, and Fe(III)–(Na, K, Mg, Ca)Cl_n–H_2O at 298.15 K. Z. Phys. Chem. **218,** 1089–1127 (2004)
22. Majima, H., Awakura, Y.: Water and solute activities of H_2SO_4–$Fe_2(SO_4)_3$–H_2O and HCl_3–$FeCl_3$–H_2O solution systems: Part I. Activities of water. Metall. Trans. B. **16B**, 433–439 (1985)
23. Dickson, A.W., Wesolowski, D.J., Palmer, D.A., Mesmer, R.E.: Dissociation constant of bisulfate in aqueous sodium chloride solutions to 250°C. J. Phys. Chem. **94**, 7978–7985 (1990)
24. Rush, R.M., Johnson, J.S.: Osmotic coefficients of synthetic seawater solutions at 25 °C. J. Chem. Eng. Data **11**, 590–592 (1966)
25. Söhnel, O., Novotný, P.: Densities of Aqueous Solutions of Inorganic Substances. Elsevier, Amsterdam (1985)
26. de Laeter, J.R., Böhlke, J.K., De Bièvre, P., Hidaka, H., Peiser, H.S., Rosman, K.J.R., Taylor, P.D.P.: Atomic weights of the elements. Review 2000 (IUPAC Technical Report). Pure Appl. Chem. **75**, 683–800 (2003)
27. Zdanovskii, A.B.: Trudy Solvanoi Laboratorii **6** Akad. Nauk SSSR (1936)
28. Clegg, S.L., Seinfeld J.H.: Improvement of the Zdanovskii-Stokes-Robinson model for mixtures containing solutes of different charge types. J. Phys. Chem. A **108**, 1008–1017 (2004)
29. Yamauchi, C., Sakao, H.: Determination of water and solute activities in the H_2SO_4–$In_2(SO_4)_3$–H_2O system. Trans. Jap. Inst. Metals **28**, 327–335 (1987)
30. Yamauchi, C., Fujisawa, T., Sakao, H.: Thermodynamic properties of $Ga_2(SO_4)_3$–H_2SO_4–H_2O solution system. Trans. Jap. Inst. Metals **29**, 150–159 (1988)
31. Rard, J.A.: Isopiestic determination of the osmotic and activity coefficients of aqueous $Lu_2(SO_4)_3$ at 25 °C. J. Solution Chem. **19**, 525–541 (1990)
32. Robinson, R.A., The osmotic and activity coefficient data of some aqueous salt solutions from vapor pressure measurements. J. Am. Chem. Soc. **59**, 84–90 (1937)